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LXXXIV.—ON THE CUPRIAMMONIUM DOUBLE SALTS.

SECOND PAPER.[1]

BY THEODORE WILLIAM RICHARDS AND ANDREW HENDERSON WHITRIDGE.

The continuation of the study of the cupriammonium double salts, begun in 1891,[2] has led to the preparation of the following new compounds:

(1) $Cu(NH_3)_2ClCHO_2$.
(2) $Cu(NH_3)_2BrC_2H_3O_2.H_2O$.
(3) $Cu(NH_3)_2BrC_2H_3O_2$.
(4) $Cu(NH_3)_2BrC_2H_3O_2$.
(5) $Cu(NH_3)_2ClC_2H_3O_2$.

(1) CUPRIAMMONIUM FORMICHLORIDE, $Cu(NH_3)_2ClCHO_2$.

The bromide corresponding to this chloride has been described already by Richards and Shaw. The chloride itself was

[1] Presented at a meeting of the American Academy of Arts and Sciences, held May 9, 1894.

[2] Theo. W. Richards: Ber. d. chem. Ges., **25**, 1492; T. W. Richards and H. G Shaw: This Journal, **15**, 642; Proc. Am. Acad., **28**, 247.

obtained at the same time by these experimenters, but only in an impure state, and the present problem was to determine the conditions necessary for the preparation of the substance in a state of purity.

If any considerable amount of water is present in the materials, basic salts of copper are certain to be precipitated, and to contaminate the preparation. On the other hand, the slight solubility of cupric formiate and cupriammonium chloride in alcohol makes it difficult to avoid the admixture of these substances with the desired compound, if alcohol is used in the anhydrous condition.

The following procedure was found to be the most successful, but great care was needed to carry it out. 3 grams of crystallized cupric formiate were dissolved in just enough warm alcohol to effect solution, and 2 grams of ammonic chloride were added to the mixture. The whole was then heated to boiling, and dry ammonia was passed in until a very slight excess was present. Upon cooling and evaporation in the air, fine blue prismatic crystals separated, which were fairly pure, as the analyses show. The salt resembles in its properties the formibromide, being permanent in dry air, but at once decomposed by water. In color it is a purer blue than the formibromide, having much less of the greenish tinge.

In the analysis of the compound the copper was determined electrolytically after the substance had been evaporated with sulphuric and nitric acids. The chlorine from a new portion was weighed as argentic chloride, and the ammonia was distilled after the addition of potash. The formic acid was determined by combustion.

Analyses of $Cu(NH_3)_2ClCHO_2$.

I. 0.0862 gram substance gave on electrolysis 0.0305 gram Cu.

II. 0.0997 gram substance gave on electrolysis 0.0356 gram Cu.

III. 0.1258 gram substance yielded 0.0994 gram AgCl.

IV. 0.1285 gram substance yielded 0.1008 gram AgCl.

V. 0.1060 gram substance distilled with caustic potash required 11.75 cc. of a decinormal solution for neutralization.

VI. 0.0984 gram substance yielded on combustion 0.0241 gram CO_2.

Analyses III and IV were made from different samples; hence, they prove the definiteness of the compound.

	Found.						Average.	Calculated for $Cu(NH_3)_2ClCHO_2$.
	I.	II.	III.	IV.	V.	VI.		
Cu	35.38	35.71	....	....	....	....	35.54	35.69
NH_3	....	....	....	....	18.91	....	18.91	19.15
Cl	....	....	19.54	19.40	....	....	19.47	19.90
CHO_2	....	....	....	....	....	25.05	25.05	25.26
							98.97	100.00

(2) Ammon-Cupriammonium Acetobromide, $Cu(NH_3)_2BrC_2H_3O_2.H_2O$.

This compound is formed readily when cupric bromide is dissolved in a mixture of alcohol and glacial acetic acid, and an excess of dry ammonia gas is passed into the solution. It is essential to have the solutions concentrated. For example, 2.5 grams of cupric bromide were shaken with 13 cc. of glacial acetic acid and 25 cc. of alcohol. Upon cooling, after the addition of the ammonia which raised the temperature of the solution, the desired substance separated out. If, when passing in the gas, a black precipitate ($Cu_2Br_4[NH_3]_{10}$) falls after the solution has become dark purple,[1] the supernatant liquid should be decanted before it is allowed to crystallize. The precipitate shows the presence of an excess of cupric bromide in proportion to the acetic acid.

Ammon-cupriammonium acetobromide had already been made by Richards and Shaw; but the analyses of the compound were so unsatisfactory that no account of the substance was given in their paper. This unsatisfactoriness was due, not to any difficulty in preparing the substance in a state of purity, as in the previous instance, but rather to the great difficulty of drying the substance enough without drying it too much. The extra molecule of ammonia and the molecule of water are held very loosely, mere exposure to the air allowing

[1] Richards and Shaw, *loc. cit.*

them to escape. Especially is this the case when the substance is placed over sulphuric acid. 0.1242 gram of material, which had been exposed thus until constant in weight, yielded 0.0331 gram, or 26.65 per cent. of copper upon electrolysis. This showed that the substance had lost practically all of its extra ammonia and water, for the theoretical per cent. of copper in $Cu(NH_3)_3BrC_2H_3O_2$ is 26.87. The new salt consists of pearly flakes of a brilliant light blue color, somewhat less intense than that of the normal cupriammonium acetobromide. It is only very slightly soluble in alcohol, and is at once decomposed by water, a little of the copper going into solution. In properties and general appearance, it resembles the ammon-cupriammonium acetochloride prepared by Richards and Shaw, except that it is much less stable.

The acetic acid was determined by distillation with phosphoric acid, according to the well-known method of Fresenius. Hydrobromic and a trace of phosphoric acid which come over in the distillate were precipitated with argentic nitrate from the neutralized solution, the result being calculated as argentic bromide, since this is the greater part of the precipitate.

Analyses of $Cu(NH_3)_3BrC_2H_3O_2.H_2O$.

I. 0.3276 gram substance yielded 0.0774 gram Cu upon electrolysis.

II. 0.3902 gram substance yielded 0.0896 gram Cu upon electrolysis.

III. 0.3376 gram substance yielded 0.2365 gram AgBr.

IV. 0.2453 gram substance yielded 0.1732 gram AgBr.

V. 0.4214 gram substance yielded 0.2940 gram AgBr.

VI. 0.2600 gram substance distilled with caustic potash required 13.28 cc. of a decinormal acid solution for neutralization.

VII. 0.1528 gram substance distilled with caustic potash required 16.29 cc. of a decinormal solution for neutralization.

VIII. The distillate from a mixture of 0.1469 gram substance with phosphoric acid required 5.67 cc. of decinormal alkali for neutralization. Approximately corrected for alkalimetric equivalent of argentic phosphate and bromide obtained from distillate, this amount becomes 5.47 cc.

	Found.				
	I.	II.	III.	IV.	V.
Cu	23.63	22.97	....	....	....
NH_3	....	....	....	....	....
Br	....	....	29.81	30.04	29.68
$C_2H_3O_2$	....	....	....	....	....
H_2O(diff.)	....	....	....	....	....

	Found.			Calculated for
	VI.	VII.	VIII.	Average.	above formula.
Cu	....	....	....	23.30	23.40
NH_3	18.20	18.19	....	18.19	18.84
Br	....	....	....	29.84	29.42
$C_2H_3O_2$	....	....	22.35	22.35	21.72
H_2O (diff.)	....	....	....	6.32	6.62
				100.00	100.00

It is evident that most of the substance analyzed had lost some of its ammonia and water. A few other determinations were made of substance just prepared and not dried at all, in order to be sure that the atomic ratio of the ammonia to the copper was not greater than 3 : 1. This point was proved beyond a doubt.

(3) Cupriammonium Propionobromide,

$$Cu(NH_3)_2Br.C_3H_5O_2.$$

10 grams of ammonic propionate, made by neutralizing propionic acid with ammonia gas and allowing the solution to evaporate over caustic potash, were mixed with 2 grams of cupric bromide, and dissolved in about 50 cc. of absolute alcohol. Dry ammonia gas was passed into the solution, and on standing, a precipitate of cupriammonium bromide

$$Cu[NH_3]_2Br_2,$$

came down. 4.5 cc. of strong propionic acid were added to dissolve the precipitate, and more ammonia gas was added. Again the same crystals appeared, showing that the tendency to form this substance was much more decided than the tendency to form the substance desired. Since the addition of more propionic acid did not help the matter, 1.5 grams of precipitated cupric oxide were added, and the whole was warmed until most of the powder had dissolved. After filtration and evaporation in the air, prismatic crystals of a very strong blue

color were deposited, proving to be the substance sought. The crystals were washed with alcohol, and dried in the air, in which they are permanent. 0.5750 gram of the substance was found to displace 0.2197 gram of toluol having a specific gravity of 0.8619; hence, the specific gravity of cupriammonium propionobromide is 2.255. The other properties resemble so closely those of the acetic compound that it is not worth while to detail them.

Analyses of $Cu(NH_3)_2BrC_3H_5O_2$.

I. 0.1017 gram substance gave on electrolysis 0.0262 gram Cu.

II. 0.1061 gram substance gave on electrolysis 0.0270 gram Cu.

III. 0.0825 gram substance yielded 0.0624 gram Ag.Br.

IV. 0.0788 gram substance distilled with caustic potash, required 6.19 cc. of decinormal acid for neutralization.

V. 0.1109 gram substance yielded 0.0588 gram CO_2 upon combustion.

	Found.						Calculated for above formula.
	I.	II.	III.	IV.	V.	Average.	
Cu	25.76	25.45	....	....	....	25.60	25.37
NH_3	....	....	....	13.40	....	13.40	13.61
Br	....	....	32.18	....	....	32.18	31.90
$C_3H_5O_2$	....	....	....	....	29.31	29.31	29.12
						100.49	100.00

(4) Cupriammonium Lactobromide, $Cu(NH_3)_2BrC_3H_5O_3$.

This compound is easily obtained by dissolving syrupy lactic acid and about a third of its weight of cupric bromide in alcohol, and then passing dry ammonia gas into the solution. Basic salts of copper do not form readily here, but if an insufficiency of lactic acid is added, $Cu(NH_3)_2Br_2$ will crystallize out. The crystals are of a strong light blue color, with a faint tinge of purple; they may be obtained of great size. They are permanent in the air, and at once decomposed by water. 2.6377 grams of the substance were found to displace 1.0334 grams of toluol, indicating a specific gravity of 2.20.

For analysis the salt was washed twice with alcohol, and pressed between filter paper.

Analyses of $Cu(NH_3)_2BrC_3H_5O_3$.

I. 0.1742 gram substance gave on electrolysis 0.0418 gram Cu.

II. 0.1108 gram substance yielded 0.0786 gram AgBr.

III. 0.1916 gram substance yielded 0.1360 gram AgBr.

IV. 0.0850 gram substance required on distillation 6.25 cc. of decinormal acid solution for neutralization.

V. 0.0987 gram substance required 7.38 cc. of decinormal acid.

VI. 0.1634 gram substance yielded on cumbustion 0.0819 gram CO_2.

Analyses II and III were made from different samples of the substance.

	Found.							
	I.	II.	III.	IV.	V.	VI.	Average.	Calculated for above formula.
Cu	23.99	....	....	....	....	....	23.99	23.85
NH_3	....	....	....	12.56	12.84	....	12.70	12.79
Br	....	30.19	30.20	....	....	....	30.19	29.99
$C_3H_5O_3$	....	....	....	....	....	33.79	33.79	33.37
							100.67	100.00

(5) CUPRIAMMONIUM LACTOCHLORIDE, $Cu(NH_3)_2ClC_3H_5O_3$.

4 grams of cupric lactate were dissolved in strong alcohol, and when the solution was boiling, 2 grams of ammonic chloride were added. Through this solution, perfectly dry ammonia gas was passed until slightly in excess. Upon filtering and evaporating the solution, fine crystals of cupriammonium lactochloride were deposited. A similar method would have answered in the case of the bromide. These crystals are of a somewhat lighter blue color than the lactobromide, but otherwise their properties are similar. Because of this similarity, determinations of the chlorine and copper were considered enough to identify the compound.

Analyses of $Cu(NH_3)_2ClC_3H_5O_3$.

I. 0.1751 gram substance gave on electrolysis 0.0496 gram Cu.

II. 0.1341 gram substance gave on electrolysis 0.0382 gram Cu.

III. 0.1314 gram substance gave on electrolysis 0.0378 gram Cu.

IV. 0.1025 gram substance yielded 0.0659 gram AgCl.

V. 0.1015 gram substance yielded 0.0656 gram AgCl.

	Found.						
	I.	II.	III.	IV.	V.	Average.	Calculated for above formula.
Cu	28.83	28.49	28.76	....	....	28.52	28.64
Cl	....	....	....	15.93	15.98	15.95	15.96

Attempts were made to make similar compounds of butyric acid without success. Various different proportions, suggested by those required in the previous preparations, were tried with uniform failure, and the attempts were finally discontinued.

It was also hoped that such compounds as $Cu(NH_3)_3ClNO_3$ and $Cu(NH_3)_2NO_3.C_4H_7O_2$ might be formed. The results of a great many experiments showed that under ordinary conditions nothing but $Cu(NH_3)_2Cl_2$, or $Cu(NH_3)_4(NO_3)_2$ can be obtained. Further attempts to combine cupriammonium sulphate with cupriammonium acetate were also unsuccessful; so that in these directions the field seems to be limited. All of these facts, as well as the relative properties of those compounds which have been prepared, may be of some use in the future when the structure of the cupriammonium compounds comes under consideration. Work upon the subject, as well as upon similar investigation of products containing amines instead of ammonia, is being continued here.

CAMBRIDGE, MASS., *September*, 1894.

LXXXV.—THE COMPOSITION OF ATHENIAN POTTERY.

BY THEODORE WILLIAM RICHARDS.

At the request of Mr. Edward Robinson, of the Boston Museum of Fine Arts, several analyses of ancient Athenian pottery were recently made at this laboratory. While the interest of these analyses was mainly archeological, turning upon the question of the identity of the source of these remains with that of others found in other cities,[1] a brief

[1] Catalogue of Greek, Etruscan, and Roman vases, Museum of Fine Arts, Boston, page 35.

statement of the results may not be uninteresting to those working upon the subject of clays in general.

The color of the broken pottery was usually pale red; the black or transparent glaze upon the outside surfaces was always very carefully scraped off before the material was pulverized. For much of the work, I am indebted to Messrs. J. A. Widtsoe and Howard Lyon; in every case the name of the analyst is recorded below.

Sample 1.—Fragment of a vase. Platinum vessels were used almost exclusively in the execution of this analysis. 1.0745 grams of the finely powdered specimen yielded 0.6015 gram of silica, 0.2771 gram of mixed ferric and aluminic oxides, 0.0651 gram of calcic oxide, and 0.1373 gram of magnesic pyrophosphate. The iron required for oxidation, 11.60 cc. of a permanganate solution, of which 1 cc. corresponded to 0.0056 gram of iron. The small amount of residue from the silica, after treatment with hydrofluoric acid, was fused with acid potassic sulphate and added to the filtrate containing the remainder of the bases.

2.184 grams of the powder yielded 0.1317 gram of mixed sodic and potassic chlorides, and these yielded 0.3173 gram of potassic chloroplatinate.

0.8843 gram of clay lost 0.0062 gram at 105° and 0.0293 gram more at a red heat.

Results, Analysis I, [Richards].

Silicic oxide	56.00 per cent.
Aluminic oxide	17.15 "
Ferric oxide	8.64 "
Baric oxide	trace
Calcic oxide	6.05 "
Magnesic oxide	4.63 "
Potassic oxide	2.80 "
Sodic oxide	0.84 "
Water at 105°	0.70 "
Water at red heat	3.31 "
	100.12 "

The other partial analyses given below were made with the intention of finding out if there were any great variations in the relative proportions of the different oxides in different samples. They were made in glass vessels; hence, in each case the total result is probably too high.

Sample 2.—Handle of a vase. Specific gravity = 2.193.

	Widtsoe.	Lyon.	Average.
Silica	54.24	54.01	54.12
Residue from silica	0.58	0.30	0.44
Alumina	17.99	18.45	18.22
Ferric oxide	9.88	10.04	9.96
Lime	6.03	6.04	6.04
Magnesia	5.46	5.49	5.48

Sample 3.—Fragment of a jar.

	Widtsoe.	Lyon.	Average.
Silica	56.57	56.65	56.61
Residue from silica	1.36	0.78	1.08
Alumina	18.11	18.01	18.06
Ferric oxide	8.12	8.62	8.40
Lime	5.05	5.17	5.11
Magnesia	....	4.40	4.40
Potash	2.98	....	2.98

Sample 4.—Fragments of a vase; and
Sample 5.—Neck of a vase:

	4. Widtsoe.	5. Widtsoe.
Silica	56.79	57.08
Residue from silica	0.37	0.57
Alumina	14.82	16.80
Ferric oxide	9.03	8.23
Lime	5.95	4.85
Magnesia	4.86	5.09

The variations in the relative amounts are singularly small, the range being not nearly so large as that given by Brougniart, in his "Traité des Arts Céramiques." Hence, it is probable that all of these specimens, which were picked up in the city of Athens itself, were the product of a local pottery.

CAMBRIDGE, MASS., *January*, 1895.

A REDETERMINATION OF THE ATOMIC WEIGHT OF YTTRIUM.

BY HARRY C. JONES.

The separation of those elements which occur together in such minerals as gadolinite, samarskite, etc., has always been a matter of considerable difficulty, due largely to the close agreement in the properties of the elements in question.

As a consequence of this, what were at one time supposed to be elementary substances, have since been shown to be mixtures of two and in some cases of a group of elements, whose compounds were so closely allied in properties as to escape the chemical methods of separation which had been employed.

Spectrum analysis, which has been so fruitful in other fields, has been of value here in showing that the substances which were supposed to be individuals were really mixtures. The atomic weights of these rarer elements have been determined from time to time by analyzing their compounds which were thought to be pure, with the result that widely different values have been found for the same element, by different experimenters using different preparations of what was regarded as the same substance. This is well shown in the case of yttrium, whose atomic weight as determined varies from about 105 to 89.1 This is not surprising, since it seems now to be pretty well established that only in one or two cases has even a fairly pure yttrium compound been obtained and used.

This but serves to show that, while the atomic weight of most of the more common elements can be regarded as known to within comparatively narrow limits, the atomic weight of some of the rarer elements may not yet have been correctly determined to within several units.

We need better methods for separating these mixtures that we may obtain purer compounds from which the atomic weights of the elements can be determined, and any step which will aid us in this direction cannot be without some interest and value.

A method more satisfactory than any hitherto employed for separating yttrium from many of the constituents which occur with it seems to have been found by Professor Rowland in connection with his study of the spectra of the rarer elements. Although an account of this method has already been published,[1] yet it is desirable to cite here that part of it which has to do directly with the separation of yttrium by the use of potassium ferrocyanide.

"This is the most useful process and easily separates the

[1] Johns Hopkins Univ. Circular, **112**, 73; reprinted in Chem. News, **70**, 68.

element (yttrium) pure and free from all others. To obtain pure yttrium from the mineral gadolinite, fergusonite, or samarskite: First obtain the crude mixed earths in the usual manner; then separate the cerium, group as usual until the absorption bands of neodymium no longer appear. For the complete separation without loss this must be done several times, as much of the yttrium group is carried down with the first precipitate. * * * * * *

"The separation of the yttrium from the other elements is effected by precipitating the latter from a weak acid solution by potassium ferrocyanide. For this purpose the filtrate, after separating the cerium group, can be used at once by slightly acidulating with nitric acid, diluting, and adding a weak solution of potassium ferrocyanide. No precipitate should appear at once, but on standing for an hour or so some will come down. Add more potassium ferrocyanide and repeat until the filtrate no longer shows the bands of so-called erbium. After this it is best to precipitate with oxalic acid or potassium oxalate, and ignite the precipitate so as to get the earth. Dissolve this in nitric acid and add only water enough to make a very concentrated syrupy solution. Place in a beaker at least three inches in diameter and examine with a spectroscope of low power for absorption bands. Probably the bands of neodymium and "erbium" will appear. Separate the first by sodium sulphate as usual, and the last by potassium ferrocyanide from an acid solution as above. The filtrate will then contain the pure yttrium, whose calcined oxalate will be pure white without trace of yellow. After separation of iron, calcium, and, possibly, manganese, the earth will be a pure element, as far as I can tell, spectroscopically. However, like Zr, Fe, and many other substances, the addition of Na or K to the electric arc, while obtaining the spectrum, will change the intensity of certain lines of the spectrum, while others are unchanged. If this is considered as evidence of the existence of two elements, then the same evidence will apply to Fe and Zr. The reason for believing that the substance thus found is an element is based on the fact that its spectrum remains unaltered in all minerals and after all chemical operations that I have been able to devise.

Furthermore, I believe that the new process is not only more easy than any other but also that it has given a single element for the first time. * * * The yield will, of course, depend on the amount of purity required. From the earths of gadolinite about one-tenth of quite pure yttrium can be obtained and about one-twentieth of very pure.

"I have determined spectroscopically that when, by the above process, the absorption band of "erbium" at last disappears from 3 inches of strong solution, all the other elements have also disappeared.

"By taking the first precipitate several times by potassium ferrocyanide from an acid solution, a mixture of many elements is obtained which contains much of that element to which the so-called "erbium" band is due. By dissolving a weighed quantity of this mixture in nitric acid and water, and examining the band spectrum, I have determined the limit when the band can no longer be seen. Thus I have proved that when the band vanishes from 3 inches of concentrated syrupy solution of yttrium there cannot exist in it more than $\frac{1}{2}$ per cent. of the mixed element as compared with the yttrium, and there is probably less.

"I have not found potassium ferrocyanide useful in the further separation of the elements, but only in separating out *a* (yttrium) from the others.

"When the neodymium band has disappeared by use of sodium sulphate, all the other elements of the cerium group have disappeared. The element thorium is sometimes present in the crude earths, but disappears after a while from the purified earths. The conditions for its disappearance I have not determined."

A specimen of yttrium oxide, purified by the above-described process, was furnished me by Prof. Rowland for the purpose of determining the atomic weight of yttrium. While the yttria was free from all other rare elements with certainty to within $\frac{1}{2}$ per cent., and probably to within much less, yet the spectrum showed that it might contain traces of calcium, magnesium, iron, and manganese. To remove the traces of these impurities, if present in the yttria, the latter was dissolved in strong nitric acid and the excess of acid evaporated

off on the water-bath. The slightly acid solution was then diluted with a large volume of water and the yttrium precipitated from the hot solution by ammonia from which all carbonate had been removed, as yttrium hydroxide. The hydroxide precipitated in this manner is somewhat gelatinous but is more easily filtered and washed than when precipitated from a cold solution. To wash the yttrium hydroxide thoroughly was a somewhat tedious process. The precipitate was allowed to settle and the supernatant liquid decanted as completely as possible. The precipitate was then treated again with hot water, well shaken, and allowed to settle. The water was again decanted and the process repeated many times until the precipitate seemed to have been well washed. A small quantity of the hydroxide was then brought on the filter and washed many times with boiling water; this was removed, another small quantity filtered off and washed, and this continued until all of the yttrium hydroxide had been finally washed in this manner. By this process any calcium or magnesium would have been separated from the yttrium.

The yttrium hydroxide was then dissolved in nitric acid and the yttrium precipitated from the acid solution by oxalic acid, which had been repeatedly crystallized from cold water, as yttrium oxalate. The crystalline oxalate was brought on the filter also in small quantities, washed well with hot water, and dried in an air-bath. The dry oxalate was ignited in a platinum crucible over the blast-lamp until the pure oxide remained. In this way any iron or manganese would have been separated from the yttrium.

The yttria thus obtained from the oxalate was pure white when heated over the blast-lamp for a short time. After prolonged heating at a very high temperature it seemed to me to acquire a faint yellow tint. Another observer declared, however, that he was unable to detect a trace of yellow.

The oxide which had been heated for a short time as well as that which had been heated more vigorously, was tested for calcium, magnesium, iron, and manganese by chemical tests, but these failed to show the presence of either of the above-named elements in the yttria.

About 6 grams of yttria were thus obtained free from all the

more common elements and containing as a maximum impurity ½ per cent. of the rarer oxides. This is the yttria which was used in the following determinations.

The platinum crucible in which the yttrium oxalate was decomposed to the oxide and which was used throughout the work, was carefully cleaned, and finally, in order to remove any iron which might distill out into the yttria, was heated for a long time in the vapors of ammonium chloride.

All weighings of the platinum crucible, either when empty or when containing the yttrium compound, were made with the crucible placed within a ground-glass stoppered weighing-tube for protection from the atmospheric moisture. This was necessitated by the hygroscopic character of the anhydrous yttrium sulphate. The crucible with its contents was placed in the weighing-tube, while still warm and the tube closed. Further cooling took place in a desiccator over calcium chloride. The stopper was removed from the tube for an instant just before weighing, to insure equalization of the air pressure. All the weighings were reduced to a vacuum standard. A long-armed Becker balance was used and the accuracy of the weights insured by previous comparisons.

I. *Conversion of the Oxide into the Sulphate.*

The platinum crucible was heated over the blast-lamp to constant weight. The desired amount of yttria, which had been already well ignited, was placed in the crucible and heated again for a short time over the blast-lamp. It was then weighed, reheated, and reweighed. In no case was any loss in weight detected, due to the second heating.

The oxide in the platinum crucible was then treated with sulphuric acid of the concentration 1 acid to about 3 of water, and placed in an ordinary air-bath and warmed gently until most of the excess of sulphuric acid had evaporated. The sulphate usually began to crystallize from the solution before all the oxide was dissolved. For this reason large amounts of oxide could not be employed in any single determination, since, with large quantities, one could not be certain that all the oxide had been transformed into sulphate. In one or two of the determinations made there was some doubt on this

point, but, that the oxide was completely converted into sulphate in all of the determinations, the results of which are given below, is shown by the fact that the sulphate was found in each case to be entirely soluble in water. The crucible containing the yttrium sulphate, a little free sulphuric acid, and, probably, some acid sulphate was then placed in an air-bath of such a form that it could be more highly heated than before. This bath consisted of a cylinder of copper about 12 cm. high and 10 cm. in diameter, into the opposite sides of which two large holes had been cut and covered with plates of mica. This enabled one to see through the bath at all times. A thick plate of copper was riveted on to the bottom and allowed to project on all sides about an inch beyond the cylinder, to prevent reducing gases from the flame from entering the bath and coming in contact with the yttrium compound. The top of the bath was covered with a plate of iron and this in turn with a sheet of asbestos. The platinum crucible was supported on a porcelain triangle about an inch from the bottom of the bath. The bath was heated by two triple burners to a little above the boiling-point of sulphuric acid. This removed all free sulphuric acid and decomposed any acid sulphate which might have been present, as was shown by testing a solution of the sulphate in water with methylorange, with which acid sulphates give an acid reaction. The sulphate was heated in this bath to constant weight. That there was no decomposition of the sulphate into basic sulphate was indicated by the two facts, that constant weight was quickly established and that the resulting sulphate was entirely soluble in water.

When the anhydrous sulphate was brought in contact with water the greater part of the salt dissolved at once, while a small portion took up water and passed over into the crystalline salt with water of crystallization. The crystalline sulphate is less soluble than the anhydrous, but on heating the solution every trace of it dissolved.

A few determinations by this method were lost by accident. In one or two cases where larger amounts of oxide were employed and not a very great excess of sulphuric acid, the sulphate, when dissolved in water, was found to contain

traces of oxide. Below are the results of the ten determinations which were successfully carried to completion:

	Y_2O_3.	$Y_2(SO_4)_3$.	$3(SO_3)$.	At. wt. yttrium. {O = 16. S = 32.06.}
I.....	0.2415	0.4984	0.2569	88.89
II.....	0.4112	0.8485	0.4373	88.92
III.....	0.2238	0.4617	0.2379	88.97
IV.....	0.3334	0.6879	0.3545	88.94
V	0.3408	0.7033	0.3625	88.90
VI.....	0.3418	0.7049	0.3631	89.05
VII.....	0.2810	0.5798	0.2988	88.94
VIII....	0.3781	0.7803	0.4022	88.89
IX	0.4379	0.9032	0.4653	89.02
X	0.4798	0.9901	0.5103	88.91
Total ...	3.4693	7.1581	3.6888	
Average.....				88.94

The mean value of the ten determinations is 88.94, with a maximum value of 89.05, and a minimum value of 88.89. The atomic weight of yttrium, calculated from the total oxide used, 3.4693 grams and the total sulphate found, 7.1581 grams, is 88.94. All of the above and following calculations are based on oxygen = 16 and sulphur = 32.06; SO_3 = 80.06.

II. *Conversion of the Sulphate into Oxide.*

Yttrium sulphate was prepared by dissolving the oxide in dilute sulphuric acid and evaporating the solution to a small volume on the water-bath, when the sulphate crystallized out. The mother-liquor was then poured off and the sulphate dried by pressing between filter paper. The desired amount of the sulphate was placed in the platinum crucible, which had been heated over the blast-lamp to constant weight, and itself dried to constant weight in the cylindrical air-bath previously described, at a temperature a little above the boiling-point of sulphuric acid. The weighed sulphate was then decomposed to the oxide in the platinum crucible over the blast-lamp. During the latter part of the heating the lid was removed from the crucible and the oxide heated in direct contact with the air.

The heating was continued until the oxide had attained a constant weight and the oxide was tested in every case for the presence of sulphate. When constant weight was reached

under the conditions employed, every trace of sulphate had been decomposed to oxide.

To test the reliability of this method, a weighed amount of yttrium oxide was converted into sulphate by the method first described and then this sulphate decomposed to oxide by the method just described. If the method of decomposition of the sulphate was trustworthy then the same amount of yttrium oxide should have resulted from the decomposition of the sulphate as was originally used. Two such tests were made and in both cases the amount of oxide obtained from the sulphate agreed with the amount originally used to within a tenth of a milligram.

Below are the results of the ten determinations by this method, which were finished satisfactorily. Here also an occasional determination was lost by accident.

	$Y_2(SO_4)_3$.	Y_2O_3.	$3(SO_3)$.	$\{O=16. \atop S=32.06.\}$ At. wt. yttrium.
I	0.5906	0.2862	0.3044	88.91
II	0.4918	0.2383	0.2535	88.89
III.....	0.5579	0.2705	0.2874	89.03
IV	0.6430	0.3117	0.3313	88.99
V	0.6953	0.3369	0.3584	88.89
VI	1.4192	0.6880	0.7312	88.99
VII.....	0.8307	0.4027	0.4280	88.99
VIII....	0.7980	0.3869	0.4111	89.02
IX.....	0.8538	0.4139	0.4399	88.99
X	1.1890	0.5763	0.6127	88.96
Total....	8.0693	3.9114	4.1579	
Average.....				88.97

The mean atomic weight from the ten determinations is 88.97, the highest value found being 89.03, the lowest 88.89. The atomic weight of yttrium calculated from the total sulphate, 8.0693 grams and the total oxide 3.9114 grams, is 88.97.

The agreement between the two series of determinations is satisfactory and the atomic weight of yttrium, as determined from the oxide which I employed, is about 88.95.

Historical Sketch.

To show how widely the results of the different determinations of the atomic weight of yttrium, which have been

made, differ from one another, I give the following brief sketch:

The earliest determination was made by Berzelius[1] in 1818. From his analysis of the carbonate, Ostwald[2] has calculated the atomic weight Y = 105. Meyer and Seubert[3], from Berzelius' analysis of the sulphate, have calculated the atomic weight Y = 96.77. (O = 16.)

From the analysis of the sulphate made by Popp,[4] (1864), Ostwald has calculated the atomic weight Y = 102.13. From Popp's determination of yttrium in the sulphate by precipitation as oxalate and weighing as oxide, Meyer and Seubert have found the atomic weight Y = 101.90. (O = 16.)

From the determinations of water in the sulphate, made by Delafontaine[5] (1865), Meyer and Seubert have found the atomic weight Y = 97.86. (O = 16.) From his determinations of yttrium in the sulphate, they calculate Y = 96.64. (O = 16.)

Bahr and Bunsen[6] (1866) dissolved yttrium oxide in sulphuric acid, evaporated on the water-bath, and gradually heated above the boiling-point of sulphuric acid. From the results, Meyer and Seubert give Y = 92.80. (O = 16.) Pure oxide was transformed into basic nitrate, and in this way was found Y = 92.48.

The above determinations are now only of historic interest, since, in the light of more recent discoveries, it is almost certain that in each case mixtures of yttrium with other rare earths, some of which were known and others not suspected, were employed.

Cleve and Höglund[7] (1873) seem to have had the purest material up to their time. By converting the oxide into the sulphate, they found Y = 89.58. (O = 16, S = 32.06.)

Cleve[8] (1883) converted as pure yttria as could be obtained into the nitrate and repeatedly fractioned by means of oxalic

1 Schweigg. J., **22**, 336; **16**, 422. Pogg. Ann., **8**, 186.
2 Lehrbuch, zweite Auflage, Bd. I, 122.
3 Atomgewichte der Elemente.
4 Ann. Chem. (Liebig), **131**, 191.
5 Ann. Chem. (Liebig), **134**, 109.
6 Ann. Chem. (Liebig), **137**, 21.
7 Bihang till. Vet. Aks. Handl., 1873, I, III, No. 8.
8 Bul. Société Chimique, **39**, 120.

acid. Finally he obtained a small quantity of yttria whose molecular weight remained constant. This was separated by means of oxalic acid into four fractions, each of which gave a sulphate containing about the same quantity of yttria. 23.2091 grams of the sulphate gave 11.2568 grams of the oxide. From this follows Y = 89.1. (O = 16, S = 32.06.)

There seems to be no doubt that Cleve's yttria was the purest hitherto employed and his determination has, up to the present, been justly regarded as nearest to the true atomic weight of the element.

The value which I have found is about 0.15 of a unit lower than that of Cleve, which argues for a corresponding increase in purity in my material over that of Cleve's, since the impurities commonly present have a higher atomic weight than yttrium. The impurity in the oxide which I used, which from spectrum analysis cannot exceed ½ per cent., and is probably less according to Rowland, is very likely a remnant of the "erbium" group which was not completely separated by the potassium ferrocyanide. The true atomic weight of the element yttrium is then, in all probability, a little lower than 88.95, the value found from the yttria which I employed.

Crookes[1] has recently raised the question as to whether the atomic weight of the yttrium obtained by Rowland had been determined. The work described in this paper, which was carried out before Crookes' communication was seen, will, it is hoped, answer that question satisfactorily.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIV.,
December, 1894.

Contributions from the Chemical Laboratory of the University of Michigan.

SEPARATION OF NICKEL AND IRON.

BY E. D. CAMPBELL AND W. H. ANDREWS.

In the separation of two elements that are at all closely related chemically, such as nickel and iron, it is desirable, if possible, first to precipitate the element sought for, as it will be accompanied by only a small amount of the second element. In, by far, the greater number of methods heretofore

[1] Chem. News, **70**, 81.

proposed for separating nickel and iron, the iron is precipitated first, carrying with it more or less nickel. The amount of nickel precipitated with the iron is variable, depending upon the composition of the precipitate, the relative proportions of the two elements, concentration of the solution, and various other conditions. The recovery of this small amount of nickel, especially if much iron be present, is usually a long, tedious process. A number of processes have been proposed in which nickel is precipitated first, the principal object in these methods being to avoid the necessity of having to handle a large, bulky precipitate of iron.

Classen[1] precipitates nickel as double potassium nickel oxalate in acetic acid solution, the iron being kept in solution as double oxalate.

Thomas Moore[2] first converts both iron and nickel into double cyanides with potassium cyanide; then precipitates nickelic hydroxide by means of potassium hydroxide and bromine, leaving iron in solution as potassium ferricyanide. G. A. Leroy[3] deposits electrolytically both iron and nickel from an ammoniacal solution of their sulphates containing ammonium citrate, then by reversing the current redissolves, and reprecipitates nickel, leaving ferric hydroxide in suspension. G. Vortmann[4] recommends the direct electrolysis of the ammoniacal sulphate of nickel in the presence of suspended ferric hydroxide.

The authors have worked out the following method which, if carefully followed, will be found to give accurate and easy separation of nickel from iron: To the mixed metals in nitric acid solution, with from 20–25 cc. excess of nitric acid is added sodium pyrophosphate dissolved in warm water. The amount of sodium pyrophosphate required should be in the proportion of about 13 grams to each gram of the metal present, which will be a slight excess over what is necessary to form the double pyrophosphate. After the addition of the sodium pyrophosphate to the ferric and nickelous nitrates contained in a medium-sized Erlenmeyer flask, the

1 Ztschr. anal. Chem., *1879*, p. 189–193.
2 Chem. News, **56**, 3, 1887.
3 Chem. News, **63**, 194, 1891.
4 Monatsh, **14**, 537, 1893.

white ferric pyrophosphate first precipitated is brought into solution by cautiously adding a clear, moderately concentrated solution of sodium carbonate, agitating thoroughly until the precipitate just dissolves and the solution attains a dull, olive-green color. An excess of sodium carbonate must be carefully avoided, as the subsequent precipitation of nickel will be incomplete if this is not done.

The solution of the double pyrophosphates of nickel and iron is filtered through asbestos into a half-liter flask and nickel precipitated as brick-red nickelous xanthate by the addition to the cold solution of 2 grams of potassium xanthate, freshly dissolved in a little water. The flask is then stoppered and shaken at frequent intervals for ten minutes when the precipitation will be complete. It is then filtered through asbestos and the nickelous xanthate immediately washed with fresh 1-per cent. solution of potassium xanthate. This precipitate is dissolved off the filter with a small amount of freshly diluted (1 : 1) fuming nitric acid. After adding 2 cc. of sulphuric acid, previously diluted with a little water, the solution is boiled down until nitric acid is completely expelled and sulphuric anhydride fumes begin to rise. The nickelous sulphate thus obtained is dissolved in a small amount of water and the iron accompanying it precipitated by the addition of a slight excess of ammonium hydroxide. The ferric hydroxide is filtered out, redissolved with a small amount of dilute sulphuric acid, reprecipitated with ammonium hydroxide, and filtered, the second filtrate being added to the first. Even when the original amount of iron is large, the ferric hydroxide taken from the nickel solution seldom exceeds 0.003 gram. The ammoniacal solution of nickel sulphate is then transferred to a large platinum dish capable of holding about 200 cc.; 3 grams of disodic-hydric phosphate dissolved in water is added, together with 25 cc. of strong ammonium hydroxide and the nickel deposited electrolytically by passing through it, a current of about 0.14 amperes per 100 sq. cm. area of the dish for twelve hours. Or, the nickel in the slightly ammoniacal filtrate from the precipitate of ferric hydroxide may be determined volumetrically by means of a standard solution of potassium cyanide, adding as an indicator, silver nitrate followed

by potassium iodide, the suspended silver iodide giving an opalescence to the solution which does not clear up until all the nickel has been completely converted into potassium-nickel double cyanide.

In making test separations by the above methods, varying amounts of nickel wire of known composition were weighed out and dissolved by an assistant who then delivered them as samples strictly unknown to the operator until the analysis was completed. In this way any prejudice on the part of the operator due to a previous knowledge of the amount of nickel present was avoided, and the method given a strictly fair test. The accuracy of the recovery may be judged from the following table in which the amount of iron added, of nickel taken and recovered, gain or loss, and method for the final determination, are given :

Iron added.	Nickel taken.	Nickel recovered.	Gain or loss.	Method.
Grams.	Grams.	Grams.	Grams.	
0.2105	0.08892	0.08910	+0.00018	Electrolysis.
1.0000	0.03430	0.03435	+0.00005	"
1.0041	0.05298	0.05345	+0.00047	"
1.0043	0.10824	0.10825	+0.00001	"
2.0043	0.02690	0.02740	+0.00050	"
Grams.	Grams.	Grams.	Grams.	
1.0010	0.00100	0.00089	—0.00011	Volumetric.
1.0086	0.06578	0.06532	—0.00046	"
1.0066	0.07582	0.07583	+0.00001	"
1.0057	0.08017	0.08050	+0.00033	"
1.0071	0.09389	0.09381	—0.00008	"

On account of the satisfactory results obtained on the separation of nickel from iron with potassium xanthate, further research is being made in the use of that reagent as a precipitant.

ANN ARBOR, MICH., *December*, 1894.

RESEARCHES ON THE COMPLEX INORGANIC ACIDS.[1]

BY WOLCOTT GIBBS, M. D., *Rumford Professor Emeritus in Harvard University.*

[*Continued from p.* 91, *Vol.* 17.]

Auramin Pyrophosphates.

When a solution of double chloride of gold and sodium,

[1] Presented at a meeting of the American Academy of Arts and Sciences, held August 1, 1894.

$AuCl_4Na$, is made as nearly neutral as possible and then boiled with sodic pyrophosphate, $P_2O_7Na_4$, a very pale yellow solution is formed, which contains the auro-sodic salt discovered by Persoz, the formula of which we should now write $P_2O_7Au'''Na$. The solution of this salt gives with ammonia a white precipitate which quickly becomes yellow and crystalline. With argentic nitrate it gives a pale yellow flocky crystalline precipitate, which is very insoluble and does not blacken readily in the light. With mercurous nitrate it gives a greenish gray flocky crystalline precipitate. A nearly white curdy precipitate is formed with sulphate of luteo-cobalt; none with sulphate of croceo-cobalt. With $Pt(NH_3)_4Cl_2$ gold is reduced.

The crystalline precipitate formed by ammonia in the auro-sodic pyrophosphate solution was well washed, dried at 150°, and analyzed.

0.9665 gram gave 0.6756 gram Au = 78.44 per cent. Au_2O_3.
0.9031 gram gave 0.7003 gram Au = 78.34 per cent. Au_2O_3.
0.9665 gram gave 0.1621 gram $P_2O_7Mg_2$ = 10.73 per cent. P_2O_5.
1.0031 grams gave 0.1703 gram $P_2O_7Mg_2$ = 10.86 per cent. P_2O_5.
0.7375 gram gave 0.02286 gram NH_3 = 3.10 per cent.
0.7691 gram lost at 150° C., 0.0420 gram H_2O = 5.46 per cent.

The analyses lead to the formula

$$14Au_2O_3.6P_2O_5.14NH_3.3Na_2O + 24Aq.,$$

which requires

		Calculated.	Found.	
14 Au_2O_3	6178	78.34	78.44	78.34
6 P_2O_5	852	10.80	10.73	10.86
14 NH_3	238	3.02	3.10	
3 Na_2O	186	2.36	2.26	(diff.)
24 H_2O	432	5.48	5.46	
	7886	100.00		

The analysis is due to Dr. Morris Loeb, who assisted me in this part of my work most efficiently.

The salt does not explode at low temperatures, but on heating to a little above 170° C., a violent explosion takes place. This shows clearly that part at least of the gold is in the form of an auramin, or compound with ammonia.

The auramin pyrophosphate of sodium, on boiling with baric chloride, gives a yellow crystalline salt; with mercuric chloride, a fine pale yellow crystalline salt which becomes very distinct on boiling.

When the auramin salt is boiled with mercurous nitrate, some mercury is reduced to metal, and at the same time very characteristic white prismatic crystals are formed. Chlorhydric acid does not sensibly dissolve the pyrophosphate, but changes it to a pale yellow flocky crystalline body. Chloride of luteo-cobalt gives, on boiling, an orange crystalline salt.

When the crystalline yellow or dull orange baric salt is well washed with hot water and then filtered off, the colorless filtrate, on evaporation, gives with sodic hydrate a very distinct reaction for ammonia. Part of the ammonia in the salt must, therefore, have been in the form of ammonia, unless we admit that the auramin is decomposed under the circumstances. When treated with a cold solution of argentic nitrate, reaction sets in at once, and a fine yellow flocky crystalline salt is formed; but no trace of ammonia is obtained from the filtrate after washing the salt with cold water and separating the excess of silver. Both the barium and silver salts were partially analyzed.

The barium salt was analyzed by Mr. G. W. Patterson:

0.6472 gram gave 0.1015 gram $BaSO_4$ = 10.30 per cent. BaO.
0.6472 gram gave 0.1426 gram $P_2O_7Mg_2$ = 14.09 per cent. P_2O_5.
0.6472 gram gave 0.3900 gram Au = 67.63 per cent.

Here the ratios are 9 Au_2O_3 : $6P_2O_5$: 4BaO.

In the silver salt (Patterson):

0.7718 gram gave 0.0915 gram AgCl = 9.58 per cent. Ag_2O.
0.7718 gram gave 0.4470 gram Au = 64.98 per cent.
0.7718 gram gave 0.1584 gram $P_2O_7Mg_2$ = 13.13 per cent. P_2O_5.

The ratios are approximately 16 Au_2O_3 : $10P_2O_5$: $5Ag_2O$.

The analyses of the barium and silver salts are at least sufficient to show that no simple double decomposition takes place in either case. The formula which I have given for the gold salt is to be regarded as purely empirical, and does not explain the explosive character of the salt. No compounds

falling under the general expression $Au_2(NH_2)_nO_n$ are at present known. Dumas and Raschig give to fulminating gold the formula $NH_2.Au'''.NH$, which may be written N_2H_2Au'''. This is equivalent to $2NH_3$; the corresponding ammonium must be $N_2H_2Au'''H_3$, and the oxide of this $(N_2H_2Au''')O$. If we assume that this oxide is present in the auramin pyrophosphate which I have described, we may write the formula

$$8Au_2O_3.6P_2O_7Au'''Na.6\{(N_2H_2Au''')O\}\{(NH_4)_2O.2H_2O+ 24aq.,$$

which is reducible to the type

$$8R_2O_3.7RO+6P_2O_7R'_4+26aq.$$

As regards the deduction of the formula from the analyses, it may be worth while to give also the equations

$$6P_2O_5+3Au_2O_3+3Na_2O=6P_2O_7Au'''Na;$$
$$3Au_2O_3+12NH_3=6\{(N_2H_2Au''')O\}+3H_2O.$$

In the determination of the ammonia by boiling with KHO or NaHO, we have

$$6N_2H_2Au'''O+3H_2O=12NH_3+3Au_2O_3.$$

Auro-pyrophosphomolybdates.

When a solution of chloro-aurate of sodium, $AuCl_4Na$, is mixed with one of pyrophosphomolybdate of sodium, a dull orange-colored fine-grained crystalline precipitate is thrown down, which is almost certainly an auro-pyrophosphomolybdate of sodium. When a solution of auro-pyrophosphate of sodium, P_2O_7AuNa, is boiled for some time with 14:6 molybdate of ammonium, a pale buff-colored crystalline precipitate is formed, which is slightly soluble in boiling water, giving, however, only a turbid liquid. After washing with cold water this precipitate was dried *in pleno* over sulphuric acid. Of this salt:

0.5581 gram lost by ignition with WO_4Na_2 0.0841 gram $H_2O+NH_3+O=15.07$ per cent.

0.8123 gram gave 0.3489 gram $Au=42.94$ per cent. $=48.18$ per cent. Au_2O_3.

0.8123 gram gave 0.0837 gram $P_2O_7Mg_2=6.59$ per cent. P_2O_5.

0.6133 gram gave 0.2615 gram Au = 42:13 per cent. = 47.85 per cent.

0.2746 gram gave 0.01558 gram NH_3 = 5.65 per cent. NH_3.

0.4774 gram lost by ignition with WO_4Na_2 0.0744 gram = 15.58 per cent.

In this last analysis the salt had probably absorbed a little water. The same is true for the next:

0.6133 gram gave 0.0624 gram $P_2O_7Mg_2$ = 6.51 per cent.

If we calculate the analyses for an anhydrous salt, we find:

		Calculated.	Found.	
11 MoO_3	1584	36.07		
5 Au_2O_3	2206	50.25	50.29	50.27
2 P_2O_5	284	6.46	6.87	6.83
15 NH_3	255	5.81	5.89	
Na_2O	62	1.41		
	4391	100.00		

In the hydrated salt the ratios are nearly

$$11\ MoO_3.5Au_2O_3.2P_2O_5.15NH_3.Na_2O + 10aq.$$

The formula requires 3.93 per cent. of water. The mean of the water in the two analyses is 4.18. It is to be borne in mind that the salt could not be recrystallized, and was probably not absolutely pure. The salt does not explode on heating, but merely "puffs." Hot dilute chlorhydric acid readily dissolves it. Ammonia-water does not sensibly dissolve it, but gives an orange-colored substance which may be the corresponding auramin compound. The formula may be written provisionally

$$22MoO_3.4P_2O_7Au'''Na.6Au_2O_3.15(NH_4)_2O + 5aq.$$

More extended investigations are necessary to fix the formulas of this and analogous compounds. Analysis by Mr. G. W. Patterson.

Auramin-pyrophosphomolybdates.

When the orange-colored flocky precipitate formed by adding ammonia to auro-pyrophosphate of sodium is boiled for some time with 14 : 6 ammonic molybdate, and the whole allowed to stand with the supernatant liquid, a pale yellowish crystalline salt is formed. After thorough washing with cold

water, the salt was dried on bibulous paper and *in pleno* over sulphuric acid. For analysis it was boiled for a short time with a mixture of chlorhydric and sulphurous acids. The phosphoric acid was determined in the filtrate from the gold by magnesia-mixture, in the manner which I have pointed out in treating of the analysis of the phosphomolybdates.[1] The filtrate from the ammonio-magnesic phosphate, after adding $(NH_4)_2S$, was evaporated, filtered to separate free sulphur, and then treated with cold dilute chlorhydric acid. The precipitated MoS_3 was filtered on a Gooch filter, washed, dried at 106° C., then washed several times with carbon disulphide, dried, and weighed. Ammonia was determined by boiling with sodic hydrate and titration.

(1) 0.3969 gram gave 0.0217 gram NH_3 = 5.47 per cent.

(2) 0.5733 gram gave 0.3612 gram Au = 70.68 per cent.

(3) 0.5733 gram gave 0.1168 gram $P_2O_7Mg_2$ = 13.03 per cent. P_2O_5.

(4) 0.5733 gram gave 0.0426 gram MoS_3 = 5.57 per cent. MoO_3.

(5) 0.3499 gram lost on ignition with WO_4Na_2 0.0703 gram = 20.09 per cent.

The salt explodes on heating, but not violently. There appears to have been a slight loss on heating with sodic tungstate, and I have accordingly calculated the water by difference, all the other constituents having been determined directly. The analyses correspond to the formula

$$12Au_2O_3.3MoO_3.7P_2O_5.24NH_3 + 21aq.$$

Analysis by Mr. G. W. Patterson.

		Calculated.	Found.
12 Au_2O_3	5297	70.54	70.68
3 MoO_3	432	5.75	5.57
7 P_2O_5	994	13.23	13.03
24 NH_3	408	5.44	5.47
21 H_2O	378	5.04	5.25
	7509	100.00	

Here, as in the cases of the other gold compounds, part of the ammonia is present as ammonic oxide and part is directly

[1] Proc. Am. Acad., 29, 64.

combined with gold ; but the proportions remain to be determined. The careful study of this class of compounds appears likely to lead to very interesting results. I have classed them only provisionally with complex acids.

As it may not be possible for me to return to the subject,[1] I will here give the results of some preliminary work, which will at least serve as starting-points for further investigation.

Molybdicotungstates.

When acid molybdate of ammonium is boiled with chlorhydric acid and potassic iodide, and the deep orange-colored liquid is precipitated with ammonia, a brown precipitate of $Mo(OH)_4$ is thrown down, which, after thorough washing, is readily soluble in a solution of 12 : 5 sodic tungstate, forming a deep orange-red liquid. Potassic bromide gives a buff-colored crystalline precipitate, which is soluble in boiling water, and crystallizes on cooling in small pale-brown scales. Ammonic chloride gives a similar salt, as do also the chlorides of barium, strontium, and calcium. All these salts are soluble in hot water, and separate from the solution in pale brown crystals. In preparing the potassium salt a large excess of potassic bromide should be used ; the bromide in this, as in many other cases, appears to be preferable to the chloride and nitrate. In these salts the molybdic dioxide may be easily and accurately determined by titration with permanganate, after adding sulphuric acid. The solutions of the molybdicotungstates readily absorb oxygen from the air, forming molybdic teroxide, a fact which must be taken into account in analysis.

Molybdic hydrate, $Mo(OH)_4$, quickly reduces MoO_3 in a solution of 14 : 6 ammonium salt, and gives a fine blue liquid, which probably contains Mo_2O_5 or $MoO_2 + MoO_3$. When a very cold solution of ammonic molybdate is employed, and molybdic hydrate is added in small portions at a time, the solution becomes yellow, then quickly green, and finally blue. It is possible that a molybdicomolybdate, $m MoO_3 . n MoO_2 . p R_2O$, is formed at first. Molybdic hydrate reduces both molybdic and tungstic teroxides in phosphomolybdates and phospho-

[1] A REBUS GERENDIS SENECTUS ABSTRAHIT.—Cicero, *Cato Major*.

tungstates. Analyses of the potassium, calcium, and barium molybdicotungstates were made with salts which perhaps were not absolutely pure. The formulas obtained appeared to be respectively

$$12WO_3.MoO_3.5K_2O + 16aq.;\ 12WO_3.MoO_3.5CaO + 32aq.;$$
$$\text{and } 12WO_3.MoO_3.6BaO + 30aq.;$$

but these are given with much reserve. In these the molybdenum was determined by titration with permanganate, and the sum of the molybdic and tungstic teroxides, after oxidation, by precipitation of the neutral solution with calcic or baric chloride. Tungstic teroxide could then be determined by difference.

It seems at least probable that tungsticomolybdates corresponding to molybdicotungstates, as, for example,

$$12MoO_3.WO_3.xRO,$$

also exist.

Uranoso-Tungstates.

When uranic oxide is dissolved in dilute sulphuric acid, and the solution is treated with metallic zinc, a solution of sulphate of uranic dioxide is formed which, after a time, deposits a gray-green powder insoluble in cold water, and, probably, a basic sulphate. This body treated with a solution of 12 : 5 sodic tungstate gives at once an olive-green crystalline salt very insoluble in hot water. The supernatant liquid has a peculiar reddish tint. The dark olive-green salt is oxidized by boiling with nitric acid and gives a yellowish-white mixture, or possibly compound, of uranic and tungstic teroxides, easily decomposed by boiling with caustic alkalies, with separation of uranic oxide and formation of sodic tungstate. A solution of 12 : 5 potassic tungstate acts in the same manner upon the uranious salt, giving also an olive-green crystalline salt and a browd-red solution. Similar results were obtained with acid ammonic tungstate. After drying for some days upon paper, the sodium salt was analyzed by Dr. Loeb:

0.4436 gram lost with WO_4NO_2 0.0331 gram = 7.46 per cent.

{ 0.9861 gram gave 0.3954 gram WO_3 = 40.09 per cent.
{ 0.9861 gram gave 0.3360 gram UO_2 and $KMnO_4$ = 34.08 per cent.

The analyses lead to this formula:

$$8WO_3.6UO_3.12Na_2O + 25aq.$$

		Calculated.		Found.	
8 WO_3	1856	39.69	74.46	40.09	74.17
6 UO_2	1626	34.77		34.08	
12 Na_2O	744	15.92		16.46	(diff.)
25 H_2O	450	9.62		9.47	
	4676	100.00			

The water determination was made by heating with sodic tungstate and determining the loss of weight. In the fusion the UO_2 is completely reoxidized to UO_3. Hence a correction must be applied to the water, which in the above case amounts to 2.01 per cent to be added. As the salt could not be recrystallized, it was doubtless not perfectly pure.

The olive-green potassium salt is also insoluble in hot water and in chlorhydric acid. It reduces silver and mercury from their nitrates, and appears to undergo double decomposition with baric and calcic chlorides. This salt was also analyzed by Dr. Loeb:

{ 1.3260 grams gave 0.4997 gram WO_3 = 37.69 per cent.
{ 1.3260 grams gave with $KMnO_4$ gram UO_2 = 33.21 per cent.

0.9275 gram lost on ignition with WO_4Na_2 0.0833 gram = 8.98 per cent.

The analyses lead to the formula:

$$8WO_3.6UO_3.9K_2O + 34aq.$$

		Calculated.		Found.	
8 WO_3	1856	37.58	70.50	37.69	70.90
6 UO_2	1626	32.92		33.21	
9 K_2O	846	17.12		16.60	(diff.)
34 H_2O	612	12.38		12.50	
	4940	100.00			

The potassic salt corresponds in constitution to the sodic salt if we write it:

$$8WO_3.6UO_3.9K_2O.3H_2O + 31aq.$$

Silico-Molybdates.

The existence of definite silico-molybdates appears to have been first observed by Parmentier,[1] who obtained potassium, sodium, and ammonium salts by the action of alkaline silicates upon alkaline molybdates in presence of nitric acid. The free acid has the formula $12MoO_3.SiO_2 + 26$ aq. I have devised another method of preparing this class of salts, which may perhaps be generalized in its application. When a solution of fluosilicic acid is poured into one of 14 : 6 molybdate of ammonium, no precipitate is formed, but the solution becomes yellow. On evaporation, a bright yellow crystalline body separates in large quantity. When normal sodic molybdate, MoO_4Na_2, is strongly acidulated with chlorhydric acid, the addition of fluosilicic acid gives at once a bright yellow color. The solution obtained in this manner gives no precipitate in the cold with ammonic chloride, but on boiling and shaking for a few minutes a beautiful bright yellow crystalline precipitate is thrown down in abundance. This is slightly soluble in hot water to a yellow liquid. A solution of fluosilicic acid mixed with one of an acid potassic molybdate forms no precipitate, but the mixture is yellow, and on evaporation to dryness upon a water-bath yields a highly crystalline yellow powder. Much molybdic teroxide is at the same time reduced to blue oxide. The yellow solutions of the silicomolybdates of potassium and sodium give with nitrate of croceo-cobalt a beautiful orange crystalline precipitate, which is insoluble in cold water and readily washed and dried. The bright yellow silicomolybdate of ammonia, after careful washing, was analyzed:

0.7963 gram lost on ignition with WO_4Na_2 0.0750 gram $NH_3 + H_2O = 9.42$ per cent.

0.5279 gram left on ignition 0.0158 gram $SiO_2 = 2.99$ per cent.

0.6504 gram gave 0.0339 gram $(NH_4)_2O = 5.22$ per cent.

0.5817 gram gave 0.03045 gram $(NH_4)_2O = 5.23$ per cent.

The analyses correspond to the formula

$$12MoO_3.SiO_2.2(NH_4)_2O + 5aq.;$$

which requires:

[1] Compt. rend., **92**, 1234; **94**, 213.

		Calculated.	Found.
12 MoO_3	1728	87.18	87.58 (diff.)
SiO_2	60	3.03	3.00
2 $(NH_4)_2O$	104	5.24	5.22 5.23
5 H_2O	90	4.55	4.20
	1982	100.00	

The silica was determined by igniting the salt with free access of air until all the molybdic oxide was expelled. The reactions of a solution of sodium salt were as follows: No precipitate with baric and calcic chlorides; none at first with potassic bromide, but, on standing, bright yellow crystals formed; a sulphur-yellow crystalline precipitate with mercuric nitrate and a beautiful bright orange-yellow highly crystalline precipitate with mercurous nitrate; a very pale yellow crystalline precipitate with argentic nitrate, and a pale yellow fine-grained crystalline precipitate with thallous nitrate. Pechard[1] has obtained the same salt by precisely the same process as that which I have employed, and has priority in publication. I have also obtained a titanio-molybdate and a zirconio-molybdate by similar methods, but have not analyzed them. Pechard has described beautiful salts of the two series, and rendered further work on my part unnecessary.

Selenoso-Molybdates.

When 24 : 1 phosphomolybdate of potassium is boiled with a solution of potassic selenite, SO_3K_2, it readily dissolves to a perfectly clear and colorless liquid, which after an hour deposits its beautiful large granular colorless crystals in abundance. These are readily soluble in hot water, and crystallize from the solution without change, except that large transparent colorless crusts are obtained. Of this salt, analyzed by Mr. G. W. Patterson:

1.1360 grams gave 0.1503 gram Se = 13.23 per cent. = 18.09 per cent. SeO_2.

1.1360 grams gave 0.7772 gram $PtCl_6K_2$ = 13.27 per cent. K_2O.

0.9570 gram lost up to 175° C. 0.0058 gram H_2O = 0.61 per cent.

[1] Compt. rend., **117**, 691-694; Cited Ztschr. anorg. Chem., **6**, 200.

Deducting the small percentage of water, the analyses correspond to the formula

$$17MoO_3.6SeO_2.5K_2O.$$

		Calculated.	Found.
$17MoO_3$	2448	68.81	68.45
$6SeO_2$	648	18.16	18.20
$5K_2O$	472	13.23	13.35
	3568	100.00	

The formula may also be written,

$$6\{SeO_3.2MoO_3\} + 5MoO_4K_2.$$

The selenium was determined by reduction with sulphurous acid and the molybdic oxide by difference. In spite of the mode of preparation, the salt did not contain phosphoric pentoxide. On repeating the preparation of the salt I obtained different results, the proportions used being probably not the same. The solution deposited at first groups of colorless crystals, and then gave, after further evaporation, a white granular crystalline salt. The grouped crystals seemed at first to be quite insoluble in water, but, when boiled, dissolved, and then crystallized out very readily. Perhaps more than one salt was formed in this operation. The solution of the salt analyzed gave pale yellow crystalline precipitate with argentic and mercurous nitrates.

Selenoso-Tungstates.

When ammonic tungstate is boiled with a solution of SeO_3H_2 it readily dissolves to a pale yellow solution, which almost immediately gives beautiful shimmering scales in a pale yellow mother-liquor. These pass at once through a filter and are difficult to separate and wash. Potassic tungstate also readily dissolves in a solution of selenious acid, forming a pale yellow solution which on heating suddenly becomes opaque, while a pale yellow precipitate is thrown down. When washed by decantation with cold water, both the ammonic and potassic salts have a distinct pale yellow color. When a solution of selenious acid is mixed with one of 12:5 sodic tungstate and a solution of potassic bromide is added, a white precipitate in very minute granular crystals is formed, settling

rather slowly, and very slightly soluble in hot water. A solution of argentic nitrate gave, with the well-washed salt, large very pale yellow crystalline flakes. Mercurous nitrate gave a pale yellow crystalline precipitate. A solution of selenious acid mixed with one of 24 : 1 : 2 sodic phosphotungstate gave a white granular precipitate very slightly soluble in hot water. After careful washing, this gave, on boiling with argentic nitrate, a perfectly white crystalline salt; a bright yellow crystalline precipitate with mercurous nitrate; and a white crystalline precipitate with baric chloride. It is possible that phospho-selenoso-tungstates are formed in this manner.

Pechard[1] has recently described salts of two series of molybdo-selenites, as he terms them, having respectively formulas which would indicate that they are derivatives of the acids $4H_2O.3SeO_2.10MoO_3$, and $2H_2O.SeO_2.5MoO_3$.

The same chemist has also described a very interesting series of salts, which he terms molybdo-sulphites, embraced under the general formula

$$4H_2O.3SO_2.10MoO_3.$$

Telluroso-Molybdates and Tungstates.

Klein[2] many years since also observed the existence of complex acids containing tellurous and telluric oxides and tungstic oxide. So far as I am aware, no analyses have been published. A preliminary notice of my own work was communicated to the Harvard Chemical Club, February 12, 1884.[3]

When a solution of $TeBr_6K_2$ is boiled with a large excess of water, the salt is completely decomposed into bromhydric and tellurous acid, TeO_2H_2. A solution of 14 : 6 acid molybdate of ammonium readily dissolves this last on boiling, and the clear filtered solution soon deposits beautiful granular colorless crystals in quantity. It is best to use an excess of tellurous acid. The telluroso-molybdate is much less soluble than the acid molybdate of ammonia, and may be redissolved and recrystallized without apparent decomposition. When a solution of the $TeBr_6K_2$ is mixed with one of the acid molyb-

[1] Compt. rend., **116**, 1441–1444; **117**, 104–106.
[2] Bull. Soc. Chim. (Paris), [2], **42**, 169.
[3] See also Ber. d. chem. Ges., **18**, 1089, August, 1884.

date, a very pale yellow precipitate is formed. After standing, small bright yellow crystals also appear. The white precipitate is probably only tellurous acid. When freshly precipitated tellurous acid is boiled with a strong solution of an acid potassic tungstate, it does not dissolve, but changes character and becomes more distinctly crystalline. A solution of $TeBr_4K_2$ gives with one of 24 : 1 : 2 phosphotungstate of sodium a very white granular precipitate, which is insoluble, and may be washed with boiling, but then settles slowly. The tellurium employed was the best commercial product, and doubtless not absolutely pure. If, as has been supposed, two different metals are embraced under the name, it is possible that the compounds of the two oxides with molybdic and tungstic oxides may afford means of separation in consequence of differences in composition and properties. Should tellurium be hereafter found to possess a technical value or interest, an abundant supply can be furnished by the mines of Colorado. The very high cost of the metal at present has prevented further study on my part.

Cerico-Molybdates.

When ceric fluoride, CeF_4, is boiled in a platinum dish with 14:6 molybdate of ammonium, the solution quickly becomes yellow, and soon deposits a fine yellow crystalline salt, which may be washed with cold water, in which it is but slightly soluble. It contains molybdic teroxide, ceric oxide, and ammonia. Basic ceric nitrate treated with a solution of hydro-potassic fluoride, KF_2H, changes character at once and becomes flocky-crystalline. After washing with cold water, boiling with 14:6 molybdate of ammonium dissolves but little, but the salt becomes bright sulphur yellow and crystalline and is practically insoluble in water. The best method of preparing this salt consists in first preparing pure basic nitrate of cerium[1] free from lanthanum and didymium (neodymium and praseo-dymium). This is to be dissolved in nitric acid and the solution diluted. Acid potassic fluoride then precipitates a nearly white flocky salt, which dissolves readily in a boiling solution of 14:6 molybdate of ammonium

[1] See my paper in Am. J. Sci., **37**, 352.

to a yellow solution, and crystallizes from this. It will probably be better to boil with a solution of an acid sodic molybdate, as this yields a soluble sodic salt, the solution of which gives with ammonic chloride a yellow crystalline precipitate of an ammonium salt, which will make a good starting-point for further investigations.

When the ceric fluorine salt, prepared as above with KF_2H, is boiled with 10 : 4 sodic tungstate, a fine bright yellow solution is formed which gives a beautiful orange, crystalline precipitate with nitrate of croceo-cobalt. In preparing the fluorine compound it is best to add a cold filtered solution of KF_2H to the basic ceric nitrate diffused in cold water, and not to heat at all. Ceric hydrate dissolves with difficulty in solutions of acid tungstates and molybdates, more easily when precipitated from cold solutions.

Note on Certain Tungstates, and on a New Phosphotungstate.

In other instalments of my work I have endeavored to show[1] that there exists a special class of metatungstates, of which the lowest term has the general formula $4WO_3.RO$, and the highest the general formula $24WO_3.11R_2O$. This view appeared to be supported both by my own work and by that of Marignac, but has not found favor with chemists, and has in fact, so far as I am aware, passed wholly unnoticed. The highest term actually obtained by me[2] appeared to have the formula

$$16WO_3.3Na_2O.4(NH_4)_2O + 18aq.$$

The only complete analysis made agreed well with this formula, and differed very materially from that of the 12 : 5 ammonia-sodic tungstate. As it has been asserted, however, that the two are identical, Mr. Charles D. Smith has made in my laboratory four analyses with portions of the salt which had been preserved. The analyses are as follows:

0.7226 gram gave 0.6038 gram $WO_3 = 83.55$ per cent.
1.1598 grams gave 0.9687 gram $WO_3 = 83.54$ per cent.
1.3281 grams gave 1.1091 grams $WO_3 = 83.51$ per cent.

[1] Proc. Am. Acad., **15**, 15. [2] *Ibid*, **16**, 76.

1.4740 grams gave 1.2309 grams WO_3 = 83.50 per cent.
1.2726 grams gave 0.0604 gram $(NH_4)_2O$ = 4.75 per cent.
1.0901 grams gave 0.0508 gram $(NH_4)_2O$ = 4.66 per cent.
1.1360 grams gave 0.0532 gram $(NH_4)_2O$ = 4.67 per cent.
0.6756 gram gave 0.0318 gram $(NH_4)_2O$ = 4.72 per cent.
4.4687 grams lost on ignition 0.5292 gram NH_3 and H_2O = 11.84 per cent.
3.0697 grams lost on ignition 0.3638 gram NH_3 and H_2O = 11.84 per cent.
4.6030 grams lost on ignition 0.5444 gram NH_3 and H_2O = 11.82 per cent.
3.3885 grams lost on ignition 0.4014 gram NH_3 and H_2O = 11.84 per cent.

The analyses correspond to the formula

$$24WO_3.5Na_2O.6(NH_4)_2O + 27aq.,$$

which requires:

		Calculated.	Mean.	I.	II.	III.	IV.
$24WO_3$	5568	83.40	83.52	83.55	83.54	83.51	83.50
$6(NH_4)_2O$	310	4.68	4.70	4.75	4.66	4.67	4.72
$5Na_2O$	312	4.65	4.65	....	....	....	....
$27H_2O$	486	7.27	7.13	7.08	7.14	7.16	7.11
	6676	100.00					

The sodic oxide is determined by difference. The analyses agree rather more closely with the new formula than with that formerly given, which I will cite for the sake of comparison:

$$16WO_3.4(NH_4)_2O.3Na_2O + 18aq.$$

This requires

		Calculated.	Found.
$16WO_3$	3712	83.77	83.94
$4(NH_4)_2O$	208	4.69	4.64
$3Na_2O$	186	4.20	4.21
$18H_2O$	324	7.32	7.21
	4430	100.00	

It is certainly difficult to decide between these two formulas, only it must be observed that the higher formula is derived from the mean of four analyses, which agree well with each other, and has therefore the weight of analytical evidence in

its favor until further research shall prove its inaccuracy. Still another formula has been proposed by Von Knorre,[1] who writes $12WO_3.3(NH_4)_2.2Na_2O + 13aq.$, which requires 84.41 per cent. WO_3, 4.73 per cent. $(NH_4)_2O$, 3.76 per cent. Na_2O, and 7.10 per cent. H_2O. The correspondence between the results of the analyses and the data required by the formula is much less than with the formula which I first gave and which Von Knorre rejects, and of course still less than with the new formula.

New Phosphotungstate.

Pure normal sodic tungstate was mixed in solution with sodic ortho-phosphate, $PO_4Na_2H + 12aq.$, in the proportion of twelve molecules of the first to one of the second salt, and chlorhydric acid added in small excess. A phosphotungstate crystallized from the solution, and was redissolved and twice recrystallized. The new salt was in fine colorless crystals, less soluble than the now well-known salt which has the formula $24WO_3.P_2O_5.2Na_2O + 27$ aq. The salt was dried on paper for analysis. It effloresced or became opaque in dry air. Mr. Charles D. Howard obtained the following results on analysis.

1.4941 grams lost on ignition with WO_4Na_2 0.1078 gram H_2O = 7.21 per cent.

1.4502 grams lost on ignition with WO_4Na_2 0.1046 gram H_2O = 7.21 per cent.

1.0950 grams gave 1.0019 grams $WO_3 + P_2O_5$ = 91.49 per cent.

1.1950 grams gave 1.0975 grams $WO_3 + P_2O_5$ = 91.58 per cent.

1.6782 grams gave 0.0720 gram $WO_3 + P_2O_5$ = 2.74 per cent. P_2O_5.

The analyses lead to the formula

$$20WO_3.P_2O_5.Na_2O.2H_2O + 19aq.,$$

which requires:

		Calculated.	I.	II.
$20WO_3$	4640	88.85	88.75	88.84
P_2O_5	142	2.73	2.74	
Na_2O	62	1.18	1.25	
$21H_2O$	378	7.24	7.21	7.21
	5222	100.00		

[1] Ber. d chem. Ges., **19**, 823.

The only 20 : 1 phosphotungstate which I have hitherto described[1] contained 6 molecules of base (BaO), and perhaps the new salt should be written $20WO_3.P_2O_5.Na_2O.5H_2O + 16$ aq. With respect to its formation with the proportions given, I may remark that I have in repeated trials failed to obtain the salt

$$24WO_3.P_2O_5.2Na_2O + 27 \text{ aq},$$

by mixing sodic tungstate and phosphate in the exact theoretical proportions and adding chlorhydric acid to the mixed solutions. The quantity of phosphate necessary to be added is much more than 1 molecule for 12 molecules of the tungstate. This remark appears to have been made by other chemists also.

Kehrmann[2] has recently described phosphotungstates which come under the general formula $18WO_3.P_2O_5.3RO$, the salts being

$18WO_3.P_2O_5.3K_2O + 14$ aq., and $18WO_3.P_2O_5.3(NH_4)_2O + 14$ aq.

He gives to the acid the name "Phospholuteo-wolframsäure"; but though there is little doubt that there is here a hitherto undescribed series, the analyses are not satisfactory.

In another part of this paper I have described three salts of a phosphotungstic acid which would have the formula

$$18WO_3.P_2O_5.6H_2O,$$

the salts themselves having respectively the formulas, $18WO_3.P_2O_5.6K_2O + 23$ aq.; $18WO_3.P_2O_5.6K_2O + 30$ aq.; and $18WO_3.P_2O_5.K_2O.5H_2O + 14$ aq.

These salts are, however, colorless, and if we admit the accuracy of Kehrmann's formulas, there must be two isomeric series. Kehrmann appears to have been wholly unacquainted with my work.

Experiments to determine the relations of WS_4K_2, MoS_4K_2, and $WS_2O_2K_2$, to phosphates and arsenates have not led to definite results, though there seemed to be a relation of some kind. The same statement applies to the various oxyfluorides of molybdenum and tungsten.

In a communication made to the British Association[3] at the

[1] Proc. Am. Acad., **16**, 127. This Journal, **2**, 282.
[2] Ztschr. anorg. Chem., **4**, 138, 386.
[3] Report for 1884, p. 670.

Montreal meeting, in 1884, I stated that complex acids existed into which platinum chloride entered, as, for instance, compounds of the type $2PtCl_4.R_2O_5$. Since then I have made various communications on the same subject to the Harvard Chemical Club. I regard these compounds as respectively phosphoric, arsenic, and antimonic oxides, in which $2PtCl_4$ replaces O_5. A great amount of work on the subject has been done, but as it is at least possible that a very different view of the subject may be taken, I will reserve the results of my work for another occasion.

NEWPORT, R. I., *August*, 1894.

[*To be continued.*]

Contribution from the Chemical Laboratory of Dartmouth College.

CUPRIC HYDRIDE.

BY EDWIN J. BARTLETT AND WALTER H. MERRILL.

In the course of experiments recently undertaken to confirm the equation for the reaction between copper sulphate and hypophosphorous acid, it was found that the quantity of hydrogen set free depends, not upon the amount of cuprous hydride formed, but upon the quantity of hypophosphorous acid present. Further investigation showed that this evolution of gas was caused by the copper sponge which results from the decomposition of cuprous hydride, and that the action continues as long as there is hypophosphorous acid present. R. Engel, in a recent article,[1] says that palladium hydride will oxidize barium hypophosphite to the phosphite with the evolution of hydrogen; and that the action is a continuous one with apparently no effect upon the hydride. This copper sponge has always been called pure copper; if so, other forms of the metal ought to react in the same manner. Copper wire, foil, and the powder formed by precipitation with hypophosphorous acid in an excess of copper sulphate solution were found to have no action upon the acid, but finely powdered cupric oxide, when reduced by hydrogen, readily oxidizes the acid. This fact would point to the conclusion that either a new hydride of copper is formed by the decomposition of cuprous hydride in the presence of hypophosphorous acid, or that this precipitate contains occluded hydrogen.

[1] Compt. rend., 110, 786.

The quantity of hydrogen in this substance was determined in the following manner: The copper sponge was first transferred to boiling water, care being taken not to remove with it any of the metallic copper which is formed upon the sides of the vessel. After thorough washing, it was boiled for half an hour to remove any traces of free hydrogen, or of the acid which might still be retained, and was then transferred to a weighed crucible. The excess of water was absorbed by filter paper and the hydride dried in an air-bath at about 60°. After weighing, it was oxidized at a dull red heat until the resulting weight was constant. The remaining copper was then determined as the oxide.

I. 0.0079 gram of the substance gave 0.0096 gram of cupric oxide.

II. 0.0088 gram of the substance gave 0.0107 gram of cupric oxide.

III. 0.0198 gram of the substance gave 0.0239 gram of cupric oxide.

IV. 0.0228 gram of the substance gave 0.0276 gram of cupric oxide.

	Calculated for CuH_2.	Found. I.	II.	III.	IV.
Copper	96.93	97.09	97.15	96.44	96.72
Hydrogen by difference..	3.07	2.91	2.85	3.56	3.28

Each of these four analyses was made with a sample independently prepared, and the agreement in the results plainly indicates that a definite compound is formed.

If this copper sponge is a fixed compound we should expect to find, as we do, that cupric oxide reduced by hydrogen has the same composition, since it acts in the same way with hypophosphorous acid. In experiments V and VI, cupric oxide was reduced in a current of hydrogen until the resulting weight was constant, then washed, and the percentage of copper determined as before:

V and VI. 0.1169 and 0.0915 gram of the substance gave, respectively, 0.1421 and 0.1111 gram of cupric oxide.

In experiments VII and VIII, the cupric oxide was reduced by hypophosphorous acid in excess until the hydride had been formed, and it, in turn, had oxidized the remaining hypophos-

phorous acid. The reaction was considered complete when hydrogen ceased to be liberated.

VII. 0.1953 gram of the substance gave 0.2362 gram of cupric oxide.

VIII. 0.0964 gram of the substance gave 0.1171 gram of cupric oxide.

	Calculated for CuH_2.	Found. V.	VI.	VII.	VIII.
Copper	96.93	97.12	97.02	96.63	97.05
Hydrogen by difference..	3.07	2.88	2.98	3.37	2.95

The above process was tested by blank experiments in which the copper powder, formed by the decomposition of cuprous hydride in a solution having an excess of copper sulphate, was used. Four determinations were made, and in each case the copper found in the cupric oxide was between 99.60 per cent. and 99.97 per cent. of the copper in the substance taken.

Properties of Cupric Hydride.

Cupric hydride, when freshly prepared, is a reddish-brown sponge-like mass, which, however, changes to a chocolate-colored powder on being freed from acid and boiled for some time. On drying, it retains this color but, if heated with a very dilute solution of hypophosphorous acid, the particles collect again into flakes and the reddish color returns. It is only when it has this appearance that hypophosphorous acid is oxidized. When heated in the air above 100°, it is unchanged, or but partially decomposed, until a heat is reached sufficient to oxidize the copper. Like the cuprous hydride, it dissolves in warm concentrated hydrochloric acid with evolution of hydrogen, but less readily, and with the formation of the cupric instead of the cuprous salt. As mentioned before, it will oxidize hypophosphorous acid to phosphorous acid, liberating hydrogen. This action was found to be a continuous one and has no effect upon the hydride, and will even take place at the temperature of the room. Böttger,[1] Graham[2] and others have shown that hydrogen, when in combination with a metal, acts as a reducing agent, especially in the cases of palladium and platinum hydrides. So in this case when

[1] Ber. d. chem. Ges., 6, 1396. [2] Proc. Roy. Soc., 17, 212.

cupric hydride is introduced into a solution where the water molecule is weakened by the attraction between hypophosphorous acid and its own oxygen, the hydride is a reducing agent of sufficient strength to destroy the remaining bond and separate the molecule. The volume of hydrogen liberated corresponds to the following equation:

$$H_3PO_2 + H_2O = H_3PO_3 + H_2.$$

When hypophosphorous acid is concentrated to a thick syrup it is decomposed by cupric hydride, giving off non-inflammable phosphoretted hydrogen and hydrogen gases. In this case the action is like that of nascent hydrogen, and, as before, the hydride appears to lose none ot its hydrogen. The acid, on the other hand, when decomposed by heat liberates spontaneously inflammable phosphuretted hydrogen, and the heat required is much greater than that used with the hydride.

Gladstone and Tribe,[1] while investigating the analogy between the action of their copper-zinc couple and hydrogen occluded by metals, found the hydrogen in combination with copper reduces a solution of potassium chlorate to the chloride, and also potassium nitrate to the nitrite and ammonia. Graham[2] says that palladium hydride will readily reduce a solution of potassium ferricyanide to the ferrocyanide. Cupric hydride formed by the action of hypophosphorous acid on a solution of copper sulphate, easily produces these reductions. With arsenious acid, however—which is also reduced by palladium hydride—there is found to be little or no action. A slight darkening in the color of the solution appeared on boiling, but did not seem to increase when more arsenious acid was added. Yet when a few drops of hypophosphorous acid were added the liquid became darker and arseniuretted hydrogen was liberated.

It has been shown[3] that the activity of the copper-zinc couple is greatly increased by ignition in a current of hydrogen gas. This increase is due probably to the formation of cupric hydride. The union of copper, zinc, and hydrogen

[1] J. Chem. Soc., **33**, 308, 1878.
[2] Proc. Roy. Soc., **17**, 212.
[3] J. Chem. Soc., **35**, 567, 1879.

was found by Gladstone and Tribe[1] to be more powerful for effecting the decomposition of certain organic substances than the electric current derived from a battery of 100 Grove's cells. Cupric hydride alone is a moderate reducing agent but, in conjunction with zinc in the copper-zinc couple, or with other oxygen-seeking substances, as hypophosphorous acid, becomes an extremely powerful reducing agent.

It has been found that hypophosphorous acid reacts with almost all the metallic oxides, either forming hypophosphites or reducing them to a metal-like precipitate, which, in several cases, already, we have found to be a definite hydride.

Contribution from the Laboratory of the University of California.

ACTION OF LIGHT ON LEAD BROMIDE.

By R. S. Norris.

In an article[2] on Double Halides, H. L. Wells mentions the fact that lead bromide is darkened by light. I had noticed the action a short time before the appearance of this article and had made a few experiments to confirm it. The discovery immediately suggested an analogy to the similar change of color in the silver halides, so an attempt was made to ascertain the nature of the action.

The darkening is much slower than in the case of the silver salts, and takes place only on the merest surface of the exposed substance; it was therefore found difficult to obtain a product all of which was darkened. This was overcome as much as possible by exposing it in a thin layer between two pieces of plate glass. The layer was formed by spreading the finely powdered bromide, as evenly as possible, over one of the plates, and then rubbing the plates together until the layer was even and transparent enough to read print through it. The plates were clamped together and exposed to the light for several days. The product was black, and on being dissolved in water, with the addition of a drop or two of nitric

[1] *Ibid.*, **31**, 561, 1877.
[2] Am. J. Sci., **45**, 134.

acid,[1] left a small amount of metallic lead, equal to about 1 per cent. of the original substance. Analysis showed the loss of 2-4 per cent. of the bromine. It seems very probable from this that the action is one of simple dissociation between the lead and bromine.

Another experiment similar to the above, using large glass plates (2×3 feet) with a space of about a millimeter between them, and exposed to bright sunlight for two weeks, gave a product lighter in color than that exposed for a shorter time, and entirely soluble in water acidulated with nitric acid. In this experiment the metallic lead which was first formed by dissociation was probably oxidized on further exposure.[2]

In order to ascertain whether pure lead bromide is decomposed by light, a small amount of the pure salt was prepared in the following manner; Lead nitrate (De Haen, puriss.) was recrystallized, and the most perfect crystals selected, washed, and dissolved in water. The solution was made strongly acid with nitric acid, and lead peroxide precipitated from it electrolytically, in a platinum dish, according to the method of Smith. The peroxide was washed by decantation, dried, and carefully heated until it was all converted into oxide, PbO. This was treated with a solution of hydrobromic acid, prepared by the direct union of hydrogen and bromine. The apparatus used in preparing the acid was entirely of glass except the roll of platinum foil over which the gases passed; and the hydrogen and bromine were both carefully purified. The lead oxide dissolved completely. The excess of acid was evaporated off, and the precipitate recrystallized from a water solution several times. The crystals which were finally obtained were assumed to be pure lead bromide. They darkened rapidly in the light.

A number of experiments were made to determine the action under different conditions. Exposed under water the action is very slow, taking several days exposure before any darkening is noticed. The fused bromide is darkened rap-

[1] In dissolving the darkened substance it was found necessary to use a little nitric acid, because dry lead bromide does not entirely dissolve in water,—presumably on account of the formation of an oxybromide.

[2] *Cf.* W. Schmidt: "The Decomposition of Lead Chloride by Light;" Ann. der Phys. Pogg., **127**, 493.

idly. Two tubes containing a small amount of lead bromide, were filled with dry oxygen and hydrogen, respectively, sealed, and exposed to the light; decomposition took place with equal rapidity in both cases, and no difference could be noticed in the action.

The evidence so far seems to be in favor of simple dissociation as the explanation of the reaction, but not enough has been obtained to furnish proof of it. I hope to be able, by further experiments, to determine whether or not this hypothesis is the correct one.

Contributions from the Chemical Laboratory of Purdue University.

XII.—THE ACTION OF AMMONIA UPON DEXTROSE.

By W. E. Stone.

The behavior of glucose toward ammonia has been studied by several investigators, but always with results that have discouraged further attention. By heating glucose with ammonia, Thenard[1] obtained a brown, amorphous body which had a bitter taste, contained varying amounts of nitrogen, and yielded up ammonia upon heating with alkalies. A similar substance was observed by Schoonbrodt[2] on treating sugar with ammonia in the presence of phosphorus pentoxide. Tanret[3] describes two liquid, basic compounds obtained by treating dextrose with strong ammonia; *viz.*, *α-glycosine*, $C_6H_8N_2$, boiling at 136°, and *β-glycosine*, $C_7H_{10}N_2$, boiling at 160.° Here it is evident that the dextrose molecule has undergone deep-seated changes. Finally, Laborde[4] noted a crystalline substance resulting when ammonia was passed over dextrose; this body did not receive further attention.

The aldehyde character of dextrose, which has been established beyond doubt, would lead us to expect a compound between it and ammonia of the class of the well-known aldehyde-ammonias. But this, as well as several other characteristic aldehyde-reactions, fails in the case of dextrose and other

[1] Compt. rend., **52**, 444.
[2] *Ibid*, **52**, 1071.
[3] Ber. d. chem. Ges., **18**, 500.
[4] Jsb. Chem., 1874, 83.

aldose sugars, notably the fuchsin-sulphurous-acid reaction and the reaction with acid potassium sulphite. The ammonia-reaction may now, however, be included in those to which dextrose and, undoubtedly, the other aldoses respond.

I have prepared a crystalline compound of dextrose and ammonia which is fairly stable under ordinary conditions and exhibits the composition and reactions of an ammonia-aldehyde compound of the formula $C_6H_{12}O_6.NH_3$.[1]

If dextrose be suspended in absolute alcohol, which has been saturated with ammonia gas, it becomes dissolved to an appreciable extent, or, if dry ammonia gas be passed into absolute alcohol in which anhydrous dextrose is suspended, solution occurs and a slight rise in temperature may be noted. Solution takes place slowly, but after standing for a week or more in a closed vessel the solution, upon exposure to the air, shows a marked sensitiveness to carbonic dioxide, the whole solution becoming turbid. If the breath or a current of carbonic dioxide be passed through the solution, immediate precipitation occurs. The precipitate is amorphous and viscous, with a sharp biting taste. After drying over sulphuric acid the substance becomes hard and brittle. It is readily soluble in water, reduces Fehling's solution strongly, gives off ammonia when warmed with alkalies and carbonic dioxide on treatment with acids. If hydrochloric acid be added to the original alcoholic solution, a flocculent precipitate is formed. Both of these substances are probably mixtures of dextrose and ammonium salts, but their precipitation, in the manner described, indicates that the dextrose is in solution, that its solubility is dependent upon the ammonia present, and that, probably, the two are in combination. By a different procedure, a definite compound of this kind has been obtained.

The alcoholic solution which has been saturated with ammo-

[1] The studies upon which this paper is based were begun by me early in the year 1894, and only after their completion as here presented did I learn of the work of C. A. Lobry de Bruyn and A. P. Franchimont (*Recueil trav. chim.*, **12**, 286–89). These authors mention the preparation of crystalline compounds of ammonia with dextrose, galactose, and levulose from alcoholic solution. The details of their work are not at hand, but inasmuch as my work presents some points not touched upon by them and has been carried on independently, I desire to publish the results and to continue the investigation, especially since upwards of two years have passed since the publication of Messrs. de Bruyn and Franchimmont without any new announcements from them.

nia and stood over dextrose, with frequent agitation for upwards of ten days, is decanted into a separate vessel and kept closed from the air. In from ten to fourteen days more, there begins a deposition of warty crystal growths upon the walls of the flask. These increase gradually until they finally converge, and flocculent crystalline masses are formed throughout the liquid. The entire process, from beginning to end, occupies about a month. On filtering off the product, the alcoholic liquid is found to be no longer sensitive to the carbonic dioxide of the air, but when allowed slowly to evaporate in a desiccator, it deposits a considerable quantity of an amorphous substance which has not been further studied. It is evident, however, from this that not all of the dissolved dextrose is transformed into the crystalline product. The yield of crystals is not large; 250 cc. of alcohol saturated with ammonia, as described, and acting upon 15 grams of dextrose, yielded about 5 grams of the crystalline material. The undissolved dextrose was gradually changed into a brown, viscous mass which has not been further investigated.

The crystalline product referred to is snow-white, and apparently stable under ordinary conditions. It is sweet to the taste, readily soluble in water, reduces Fehling's solution readily, and might be mistaken for a specimen of pure anhydrous dextrose. It is insoluble in cold alcohol and ether, but may be dissolved in 80-per cent. alcohol upon warming. An aqueous solution of the compound shows an alkaline reaction with litmus paper. Ammonia is given off on warming with caustic soda, or when the material is strongly heated by itself.

The material melted sharply between 122° and 123° (uncorr.). The percentage of ammonia was determined by distilling with caustic soda into standardized acid. In this way 8.74 per cent. of ammonia was obtained from a freshly prepared sample. For the compound $C_6H_{12}O_5.NH_3$, the theoretical percentage of ammonia is 8.63, and for a compound of the hydramid class, $(C_6H_{10}O_5)_3N_2$, 6.53 per cent. This leaves little doubt as to the nature of the compound, and this conclusion is further supported by its general behavior.

The specific rotation in watery solution was found to be $(\alpha)_D = 22°$ to 22.7°. No birotation was observed. In this

connection it is of interest to recall the observation of Tollens, that small quantities of ammonia added to solutions of sugars which normally exhibit bi- or multirotation, destroyed this property at once.

Apparently, this compound is stable at ordinary temperature, although analysis of a preparation, about a month after its separation from the alcoholic solution, showed 8.03 per cent. of ammonia, but this had not perceptibly decreased after another month.

The union of the ammonia with the dextrose molecule seems to protect it against certain general reactions, or at least delay them until the ammonia has been displaced, as the following observations will show: A carefully prepared fermentation-experiment, in which some pure dextrose was checked against the ammonia derivative, showed that while the dextrose fermented almost completely in the first twenty-four hours, the ammonia compound was quite unaffected until about thirty-six hours, and the fermentation went on slowly for more than a week. At the end of this time the degree of fermentation was practically the same as that of the pure dextrose but it was, without doubt, much less susceptible to the action of the yeast at first.

Its reducing power toward Fehling's solution was also studied: In 1-per cent. solution, titrated into undiluted Fehling's solution, 5.7 mgrs. of the substance were required to precipitate all of the copper from 1 cc. of the solution. This is appreciably less than the reducing power of dextrose, which is 4.753 mgrs. to one cc. of Fehling's solution. It was also noticeable that a longer period of boiling was necessary than under the ordinary conditions. This shows that the dextrose molecule is regenerated from the ammonia compound by the action of the alkali, and then behaves toward the Fehling's solution in the ordinary way.

It was of especial interest to study the behavior of this compound toward phenylhydrazine, which gives such characteristic products with dextrose. Upon treating 0.5 gram of the substance with phenylhydrazine chloride and sodium acetate in the manner prescribed for the preparation of dextrosazone,

[1] Ber. d. chem. Ges., **26**, 1799,

no reaction occurred at 60°, and only after heating for some time at 100° did the characteristic yellow precipitate appear. This is in marked contrast with dextrose, which reacts readily at from 80° to 90° in a short time. The reaction of dextrose with phenylhydrazine in the cold, by which dextrose-phenylhydrazine is formed, was also studied: Equal parts of the ammonia compound, of water, and of phenylhydrazine were mixed and kept at ordinary temperature for ten days or more without perceptible reaction taking place. A corresponding preparation with pure dextrose gave the characteristic crystalline compound within four days. Here it is noticeable that, in the absence of sufficient heat to decompose the compound, the aldehyde group was protected against the action of the phenylhydrazine to which it is usually so susceptible.

By the action of hydrogen sulphide upon the aldehyde-ammonia compounds, are produced the *thialdines*. A study of this reaction, as applied to the dextrose-ammonia derivative, indicates that a sulphur compound is also formed, but no definite conclusions have yet been formed as to its exact nature. A watery solution of the substance was saturated with hydrogen sulphide, and on being allowed slowly to evaporate in the air a small quantity of needle-shaped crystals were observed. Some of the original alcoholic solution of the compound, before it had begun to crystallize, was also saturated with hydrogen sulphide, and after standing twenty-four hours there had separated out a granular, pale yellow precipitate. On exposure to the air and evaporation of the ammonia the yellow color of the solution disappeared and needle-shaped crystals were formed. These crystals were soft and flexible and easily melted. The material had an intensely disagreeable odor, and, on burning, gave off sulphur dioxide. When introduced into boiling Fehling's solution there was an immediate precipitation of cupric sulphide, but no reduction of copper was noted. The compound was wholly soluble in water but insoluble in alcohol, ether, and carbon disulphide. A determination of sulphur yielded over 30 per cent., but as the material was not pure this has not much significance.

An attempt was made to form salts which would seem possible from the basic nature of the compound. It is possi-

ble that the precipitates from alcoholic solution already mentioned as formed by the action of carbonic acid and hydrochloric acid were of this nature, but they also evidently contained ammonium salts of these acids also. A watery solution, to which had been added an excess of strong alcohol gave no precipitate with hydrochloric acid. Upon adding to this an alcoholic solution of platinic chloride, an immediate precipitate was formed, but this, upon separation and analysis, proved to be ammonio-platinic chloride. This would indicate that the compound is decomposed in the presence of acids.

Aside from the interest connecting to this characteristic aldehyde-reaction for dextrose, this new compound indicates the possibility of some new derivatives of the aldose sugars which will repay study. I am at present occupied with the extension of the reaction to other related sugars, and also with the investigation of some of their derivatives.

XIII. THE CARBOHYDRATES OF THE GUM OF ACACIA DECURRENS.

By W. E. Stone.

The so-called gums, such as gum-arabic, cherry gum, peach gum, etc., which are secreted from plants probably as the result of pathological conditions are, so far as studied, capable of conversion into the sugars of the mono-saccharide group. It is perhaps too much to say that these stand in a similar relation to the sugars as do the starches and celluloses, but at least such a relation is suggested by their easy transformation into sugars by what is apparently a breaking down of complex bodies into those more simple. In some cases the gums seem to be composed of more than one kind of such sugar-producing bodies. So, for instance, gum-arabic, obtained from various sources but understood to be from certain species of acacia, yields upon hydrolysis both arabinose and galactose. The gum exuded from the bark, as well as the fruit of the peach tree also yields upon hydrolysis both arabinose and galactose. The gum of the cherry consists chiefly of the substance from which arabinose is derived. In all of these cases the gum seems of homogeneous character and,

aside from the ash-constituents which they invariably contain, no different classes of components can be isolated from them. It is not even clear in what way these differ from the insoluble constituents of plants which yield similar sugars. For instance, all of the gums which have been well studied yield arabinose and galactose. The isomer of arabinose, xylose, is never derived from this kind of material, but only from the insoluble pentosan known as xylan. Galactan, however, is gotten indifferently from both gums and the insoluble galactan found in seed coats and similar tissues. What part these gums play in the economy of the plant is also not understood, although gumosis is thought to be either a perversion of tissue-building materials from their normal function, or a direct degeneration of tissues already formed. These bodies therefore still offer much of interest to the investigator.

Some time since I received from Professor W. T. Swingle, of the United States sub-tropical experiment station at Eustis, Florida, a sample of gum which had exuded from a specimen of the Australian black wattle, *Acacia decurrens*. The sender noted that he had never before observed gumosis in this tree, and suggested a connection between the gum and the tannin which is produced so abundantly by the tree.

The gum was in the form of transparent, amber-colored masses, which were very hard and brittle. It was slowly soluble in water at ordinary temperature, forming a mucilage. Solution occurred more rapidly if a dilute solution of caustic soda was employed. The aqueous solution was slightly acid in reaction and distinctly levo-rotatory in its effect upon polarized light. Both basic lead acetate and strong alcohol precipitated from this solution a flocculent white precipitate. These characteristics are all like those exhibited by the gums already referred to.

The gum did not melt upon heating. At from 200° to 230° it blackened, and on ignition an appreciable quantity of ash remained, which was found in one case to amount to 12.17 per cent. By means of the spectroscope, calcium, potassium, and sodium were detected in this ash, and iron and sulphuric acid were also noted.

In order to determine the character of the carbohydrates present, preliminary tests were made for pentosans and for the galactose-forming group. For pentosans, one gram of gum was distilled with 100 cc. of hydrochloric acid of 1.06 specific gravity. In this distillate the furfurol was determined by precipitation with phenylhydrazine after the method of Tollens and his pupils, except that the precipitate was collected and treated according to the suggestion of Krug. The yield of furfurol was 25.42 per cent. (Tollens and Flint by practically the same method obtained 25.41 per cent. furfurol from cherry gum.)

Galactan was tested for by heating 2 grams of the gum with 60 cc. of nitric acid of 1.15 specific gravity, upon a water-bath, by which was obtained 11.39 per cent. of mucic acid which was verified by its melting-point, 213°.

These results indicated the presence in the gum of a complex carbohydrate of the galacto-araban character, already noticed in peach gum, in the seed coats of certain leguminosæ, and probably also in the coffee berry.

In order to study the products of hydrolysis more thoroughly, 80 grams of the gum were treated with 640 cc. of 2 per cent. sulphuric acid, being heated for twelve hours in a boiling water-bath. The gum became completely dissolved, but a flocculent humin-like substance was separated. After neutralizing the acid with calcium carbonate, and evaporating the solution, there remained a dark-colored, sticky syrup. This was extracted several times with boiling alcohol and these extracts on concentration finally yielded about 10 grams of impure crystals. By repeated recrystallizations from water and alcohol, three fractions of white and apparently pure sugar were obtained. The specific rotation which is the most important character in the identification of these sugars, was determined for each of the portions.

No. 1 showed strong birotation and immediately after solution this amounted to $(\alpha)_D = +150°$. After forty-eight hours the rotation became constant and was found to be $(\alpha)_D = +102.8°$. This sugar reduced Fehling's solution strongly, and its osazone melted at 158°. These results agree with the constants for arabinose, which this sugar was without doubt.

No. 2 showed a specific rotation after two days of $(\alpha)_D = +86.6°$. After recrystallization, by which a portion of the mother-liquor was lost, the rotation was $(\alpha)_D = +95°$.

A third portion of crystals showed a rotation of $(\alpha)_D = +98°$. These second and third portions were evidently mixtures of arabinose and some sugar of a lower specific rotation. In recrystallizing, it seems that the arabinose was the first to separate, and the other sugar, in the process of drying the crystals on porous porcelain plates, was lost in the mother-liquor. There is little or no doubt, however, that this was galactose, since the mucic acid obtained from the gum indicated the presence of such a carbohydrate in the material. The analogy of other gums of similar origin and character also speak for this conclusion. The specific rotation of No. 2 was also very nearly that of pure galactose, $(\alpha)_D = 83°$.

The gum of *Acacia decurrens*, therefore, does not essentially differ from gum-arabic or peach gum, or cherry gum. It furnishes an additional example of the occurrence of a galacto-araban complex.

REVIEWS AND REPORTS.

THE RISE AND DEVELOPMENT OF ORGANIC CHEMISTRY. By CARL SCHORLEMMER, LL. D., F. R. S., late Professor of Organic Chemistry in the Owens College, Manchester, Victoria University. Revised edition, edited by Arthur Smithells, B. Sc., Professor of Chemistry in the Yorkshire College, Leeds, Victoria University. London: Macmillan & Co., 1894. pp. 280.

Chemists everywhere will welcome the new edition of this extremely interesting and valuable book, which, in the Preface, Professor Smithells, the Editor, calls "a piece of work eminently characteristic of his (the author's) genius, disclosing at once the breadth and depth of his knowledge, and his ardent and disinterested love of what he was wont to term, with the pride of a disciple, 'our science.'" The Editor has written a biographical notice as an introduction, from which we learn that Schorlemmer's pupils and admirers "have decided to perpetuate his memory by erecting at Owens College a commodius laboratory (now approaching completion) for the prosecution of organic chemistry."

The book before us is probably the most readable book dealing with the history of chemistry now in existence, and it can be highly recommended to all students of chemistry.

Those who are already somewhat familiar with the subjects presented will find in it much that is suggestive. New light is thrown upon the chemical investigations and upon the most important theories of chemistry, so that the philosophy of the development of organic chemistry becomes clearer as one reads. The Editor tells us that "Schorlemmer's keen interest in the history of chemistry in which he had latterly made researches of considerable importance finally induced him to commence a book upon the whole subject. This, unfortunately, remained uncompleted at his death, but the portion which he had written, bringing the subject down to the end of last century, will be published shortly."

All the most important recent investigations in organic chemistry are skillfully summed up. The investigations of Emil Fischer, on the sugars; of Ladenburg, on the alkaloids; of Fischer and of Behrend and Roosen, on uric acid; of Von Baeyer, on indigo; and those of the same chemist on the constitution of benzene, are more clearly presented than anywhere else.

A few brief closing paragraphs of the book may appropriately find place here: "Organic Chemistry advances with giants' steps. About fifty years ago only twelve hydrocarbons were known, and twelve years ago this number had increased to about 200. To-day we are acquainted with more than 400, and many of them, as well as their numerous derivatives, have been carefully studied." "What would Gmelin say to-day? When writing his *Handbook* in 1827 he requested chemists to cease their discoveries that he might finish his work." To this the author appends the following foot-note: "When, in 1829, it was found that pyrouric acid and cyanuric acid were identical, Wöhler wrote to Liebig: 'Gmelin will say, Thank God, one acid less.'"

One who is inclined to be appalled by the mass of material dealt with under the head of organic chemistry, will be cheered by these words: "But in spite of the grand development of chemistry, nay, even for this reason, a survey becomes easier from day to day. The large chapters of former handbooks, treating of coloring matters, bitter principles, indifferent compounds, and other bodies, which could not otherwise be arranged in the system, and which Gerhardt called 'corps à sérier', become shorter and shorter, and will disappear in the course of time." I. R.

GRUNDZÜGE DER MATHEMATISCHEN CHEMIE. DR. GEORG HELM. Leipzig: W. Engelmann, 1894. 138 pp. Price, 3 marks.

In Helm's Outlines of Mathematical Chemistry we have for the first time a logically arranged presentation of the beautiful

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energy theory of chemical changes and chemical equilibria. The little book is essentially a modern production, for its subject-matter is up to date and its method is that of the energy theory, pure and simple. It deduces in orderly sequence the known relations of chemical phenomena, and it omits those unknown things which we call hypotheses.

The material which is introduced has been selected wisely, for no important element of the theory has been omitted; and yet the subject has been kept within proper limits by avoiding any undue elaboration of the fundamental formulas, and, above all, by a really scientific employment of the economy of expression which mathematical description affords. The mathematical means which are employed are nevertheless exceedingly simple, so that one is reminded still more forcibly than usual of the very true saying that "It is easier to learn the calculus than to understand a demonstration which avoids its use." It has certainly become impossible to read chemical theory without a working knowledge of the calculus.

The first part of Helm's book treats the conservation of energy, the conception of the store of energy of a body, the significance of energy differences, and the various forms in which quantities of energy appear. The resolution of such forms into their intensity and quantity factors is effected in the second part, and the simpler theorems of thermodynamics are derived. In the third part we find a charmingly simple exposition of the theory of the thermodynamical potential (the theory of affinity) comprising among its applications the general theory of chemical equilibrium, the physical theory of solutions, and the theory of the velocities of reactions. The fourth part concludes the subject by a comprehensive presentation (in only eleven pages!) of the Phase Rule of Gibbs.

To select for comment features of especial excellence from so original and consistent a treatise would be an extended task; to select details for unfavorable criticism would be a thankless one. It should, however, be stated that the author, by reason of his standing as an energy theorist, is peculiarly fitted to write such a work; nothing but good is to be said of it, and it is probably true that no existing publication is so well adapted to serve as an introduction to Physical Chemistry, as an introduction to the study of chemistry as an exact science.

J. E. TREVOR.

DIE PRAXIS DES ORGANISCHEN CHEMIKERS. DR. LUDWIG GATTERMANN, A. O. Professor an der Universität Heidelberg. Mit zahlreichen Abbildungen im Text. Leipzig: Veit & Co., 1894. pp. 303. Price, 6 marks.

This is a thoroughly practical book written by one who is a skilled experimenter and who has had much experience in

teaching organic chemistry to students in one of the busiest laboratories of the world. It differs from the much-used "Anleitung" of Emil Fischer and that of S. Levy in that it contains directions for carrying out the different kinds of operations that are necessary in organic work, such as crystallization, sublimation, distillation, extraction, drying, filtration, heating under pressure, determination of melting-points and of boiling-points. These operations are described in detail and many valuable "tricks of the trade" are presented in a thoroughly clear manner. Under the head of analytical methods are given in detail the methods in use in the best laboratories, and these are so clearly described that "he who runs may read."

The "Spezieller Teil" of the book deals with preparations after the manner of Fischer and Levy, but the presentation of the matter is somewhat more systematic than in either of these. The author has added remarks of a general character to the description of each method of preparation, with the object of giving the student something more than the mere knowledge of how to make this or that substance. He has, in fact, given us an elementary text-book of organic chemistry with experiments in the foreground. This ought to be of great value, and ought to do much towards counteracting the deplorable tendency on the part of students, even of good students, to work mechanically while in the laboratory, and to leave all reading and thinking to be done after laboratory hours. The subdivisions of the "Spezieller Teil" are I. Aliphatic Series; II. Aromatic Series; III. Pyridine and Quinoline Series; IV. Inorganic Part. All the principal reactions of the compounds of carbon are brought under the observation of the student in such a way as to impress upon his mind their general character and applicability. To illustrate, the first reaction studied is the substitution of halogen for alcoholic hydroxyl. The first example is furnished by the preparation of bromethane, and the second by the preparation of iodoethane. Then follow six pages which deal with this reaction in a general way, many examples being cited, and peculiarities in special cases being referred to. Any intelligent student working conscientiously through the course laid out must acquire a good general knowledge of organic chemistry.

I. R.

DIE MASCHINELLEN HILFSMITTEL DER CHEMISCHEN TECHNIK. A. PARNICKE. Frankfurte, a. M.: H. Beckhold, 1894. 8 vo. 320 pp.

In this well-illustrated book the author has collected and

systematically arranged, according to their several uses, the mechanical appliances usually found in large or small chemical works. Some special forms of apparatus, which may be regarded as trade secrets, are omitted, as is also apparatus of but limited application in the arts. A notable omission is the machinery used in textile coloring and printing, and the modern forms of ice machinery do not receive their proper share of treatment.

The author begins with miscellaneous subjects connected with the fitting and use of machinery, followed by interesting chapters on the transmission of power (including electric, hydraulic, and pneumatic transmission) and on transportation appliances. Disintegrating machines and mills, mixing machines, furnaces and ovens, are next considered. The chapter on concentration and evaporation contains much of interest to the technical chemist.

The eighth chapter is devoted to appliances for the mechanical separation of substances, including extraction and fractionation. Beginning with the setting of simple sieves the author passes in regular order to shaking and revolving screens, separators, presses, centrifugal machines, filter presses, sand and vacuum filters, crystallizers, extraction and fractionation apparatus. The chapter closes with a short description of the apparatus for separating gases from each other by absorption. Considerable attention is devoted to contrivances for drying and desiccation, while another chapter discusses scales and balances, thermometers, pyrometers, manometers, and dynamometers.

Finally, abstracts from the statutes and ordinances governing the construction of industrial plants and the use of industrial appliances are given. These have been made subjects of national legislation in Germany, and are not left to the judgment of a local board of aldermen, as is too often the case in this country. The prescribed penalties for infringement or disregard of the statutes are, moreover, strictly enforced in Germany.

Though intended for the use of German readers, and treating for the most part of machinery produced by German firms, the book cannot fail to commend itself also to English and American technical chemists. The explanations of the principles involved in each piece of mechanism are satisfactorily given. The descriptions of the machines are generally clear and concise, and supplemented by excellent and abundant illustrations.

FRANK H. THORP.

A TEXT-BOOK OF ORGANIC CHEMISTRY. By A. BERNTHSEN, PH.D., Director of the Scientific Department in the Chief Laboratory of the Baden Aniline and Alkali Manufactory, Ludwigshafen-am-Rhein, formerly Professor of Chemistry in the University of Heidelberg. Translated by George McGowan, Ph.D. Second English edition revised and extended by author and translator. London: Blackie and Son, Limited; New York: D. Van Nostrand Company, 1894. 596 pp.

In the preface to the first German edition of this book the author states that "In lecturing upon organic chemistry in the University of Heidelberg I have felt more and more each session the desirability of being able to place in the hands of my students a small text-book, of which the descriptive portion was condensed as far as practicable and yet which should be of a strictly scientific character; a book which beginning with the homologous series, should lay especial emphasis upon summarizing the characteristics of each class of compounds, and, wherever possible, upon the inductive development of the theoretical relations existing between them. The following text-book of Organic Chemistry is an attempt to fulfil these requirements." That this attempt has been attended with success may be seen from the fact that four German and two English editions have been called for within the short space of six years.

On comparing this book with the first English edition it will be seen that, while the admirable original plan of treatment outlined by the author in the quotation given above is strictly adhered to, no part of the work has been left unrevised and several chapters have been completely rewritten in accordance with our present knowledge of the subject. This applies especially to the sections dealing with stereochemical isomerism, aldoximes and ketoximes, carbohydrates, special benzene formulas, hydrogen addition-products of the phthalic acids, various dyestuffs, alkaloids, the terpenes, and camphors, as well as to those sections which deal with the determination of molecular weights by physical methods, the ketonic acids and diketones, the uric acid group, the azoles, certain naphthalene derivatives, and the quinoline and acridine groups. Certain sections of the book, like those on the sugars, the albumens, the terpenes, and physical chemistry have been revised by those who have made a special study of these subjects and whose names are familiar to all chemists through their researches.

The system of International Nomenclature agreed upon at the recent conference of chemists at Geneva has been made use of both in the text and in the index, the "official name" being generally added in brackets after the name in ordinary use.

An excellent feature of the German edition which has happily been retained in the English translation is the use of two kinds of type, so that the most important matter, either in itself or for purposes of a general review, may be readily distinguished by the reader.

The number of references given in the book, though not very large, is sufficient to call the attention of the student to points which have a particular historical value or to recent researches where space does not permit of these being given in detail. The index is very complete and is free from those errors common in the ordinary index, which are so annoying to the reader.

The book is well printed and well bound. The translation is, in general, true to the original and very clear. The book is certainly one that can be most heartily recommended to both teachers and students of organic chemistry. It is quite probable, however, that teachers of the subject will find it advisable to put a more elementary book like Remsen's Organic Chemistry into the hands of beginners in the subject.

W. R. O.

A TEXT-BOOK OF VOLUMETRIC ANALYSIS. BY HENRY W. SCHIMPF, PH.G.

This work was written with special reference to the volumetric processes of the Pharmacopoeia of the United States, for the use of pharmacists and students of pharmacy, the author's experience as a teacher having convinced him of the need of a work especially designed for this class of students. The methods appear to be well selected, and the style of the book is clear and concise.

H. N. M.

ANLEITUNG ZUR DARSTELLUNG ORGANISCHER CHEMISCHER PRÄPARATE. Handbuch der Laboratoriumstechnik, enthaltend Beschreibung der Darstellungsmethoden organischer Präparate nebst Angabe ihrer Eigenschaften und Prüfung. VON DR. HUGO ERDMANN. Stuttgart: Ferdinand Enke, 1894. 610 pp.

This book is the second volume of Bender and Erdmann's Präparatenkunde. It gives detailed instructions for making over 500 organic preparations. Dr. Erdmann says in the preface that he has carefully studied the methods of formation of all of the compounds described, and in nearly every case found it possible to improve the methods, either by simplifying them or by increasing the yield. The book is unique, without a rival. In the estimation of the present writer no chemical laboratory can afford to be without it.

E. R.

Recent Researches on Diazo-Compounds.

During the past two years the diazo-compounds have been the subject of many investigations, which have brought to light some important facts and led to extremely interesting speculations. In this article the attempt is made to present these results as briefly and as clearly as possible.

Bamberger has been occupied for some time with experiments on the oxidation of diazo-compounds.[1] By treating a solution of diazo-benzene with potassium ferricyanide, he obtained a compound of the formula, $C_6H_5N_2O_2K$, which he called potassium diazobenzenate (diazobenzolsaures Kalium), and from this the free diazobenzenic acid was separated. This acid Bamberger regards as phenylnitramine, $C_6H_5.NH.NO_2$, rather than phenylimidonitric acid, $C_6H_5.N:NOOH$. His reasons for holding this view are the following:

(1) Sodium amalgam reduces the compound to phenylhydrazine:

$$C_6H_5.NH.NO_2 \longrightarrow C_6H_5.NH.NH_2.$$

(2) The methyl ether yields methylaniline and a nitrate when treated with an alkali:

$$C_6H_5.N(CH_3).NO_2 + KOH = C_6H_5.NH.CH_3 + KNO_3.$$

(3) The methyl ether is converted, first, into methylanilinenitrosamine and then into methylphenylhydrazine, when treated with zinc and acetic acid:

(1) $C_6H_5.N(CH_3).NO_2 \longrightarrow C_6H_5.N(CH_3).NO.$
Methylphenylnitrosamine.

(2) $C_6H_5.N(CH_3).NO \longrightarrow C_6H_5.N(CH_3).NH_2.$
Methylphenylhydrazine.

(4) When treated with "bleaching powder" diazobenzenic acid is converted into an oily product with the general properties of the chlorimides. It is, therefore, probably $C_6H_5.N.Cl.NO_2$.

While this evidence is satisfactory as far as it goes, one fact established by Bamberger furnishes evidence in favor of the formula $C_6H_5.N=NOOH$ for diazobenzenic acid. He found that, when the silver salt of the acid is treated with methyl iodide, a methylether is obtained isomeric with that obtained when the sodium salt is used. As the latter breaks down readily into methylaniline and nitric acid, it is probably to be represented by the formula $C_6H_5.N(CH_3).NO_2$. It appears, therefore, that the former corresponds to the formula $C_6H_5.N=NOOCH_3$. Bamberger expresses the view that diazobenzene may react in two tautomeric forms. In one of these the true diazo grouping occurs, $C_6H_5.N=N.OH$. This, by oxidation, would yield the azo-compound $C_6H_5.N=NOOH$. The other

[1] See Ber. d. chem. Ges., **25**, 472; **26**, 482; **27**, 359.

is a nitrosamine $C_6H_5 . NH . NO$. This, by reduction, yields phenylhydrazine.

Von Pechmann[1] has also been engaged in work on the diazo-compounds and has been led to the same general conclusions as Bamberger.

Schraube and Schmidt[2] further, in an article giving the results of a very thorough and skillful investigation show clearly that, in the case of paranitrodiazobenzene, two forms exist, one of which, according to the authors, is a true diazo-compound, while the other is a nitrosamine. In the course of an investigation of the transformation products of diazoparanitraniline it was observed that, when a solution of paranitrodiazobenzene chloride is added to an alkaline liquid, for example, a dilute solution of caustic soda, so that the alkali is present in excess, a clear, yellow solution is obtained, in which, although no evolution of nitrogen takes place, not a trace of a diazo-compound can be detected. From this solution crystals separate after a time, and, by neutralizing the cold solution with acid, a yellowish, difficultly soluble, crystalline precipitate is formed. Heat decomposes this with evolution of nitrogen, while, on addition of larger quantities of acid, it passes into solution; and this solution exhibits the properties of the original diazo-compound. The authors state that the crystals which separate from the alkaline solution are the sodium salt of paranitrophenylnitrosamine $C_6H_4.NO_2.NNa.NO$; and the substance separated from the solution by addition of an acid is the free nitrosamine $C_6H_4.NO_2.NH.NO$. The evidence offered is the same in character as that offered by Bamberger. When the sodium salt is treated with methyl iodide, the nitrosamine of nitromethylaniline $C_6H_4.NO_2.N.CH_3.NO$ is formed. That the substance precipitated by acids from the alkaline solution is not free nitrodiazobenzene, $C_6H_4.NO_2.N:NOH$, but the nitrosamine $C_6H_4.NO_2.NH.NO$ is shown by the fact that it gives no color-reaction when brought into an alkaline solution of β-naphthol, and, further, by the fact that, with acetic acid, it does not form the soluble acetate of the diazo-compound, and at lower temperatures it does not form, easily soluble salts with mineral acids. The potassium salt of diazobenzene proved to be a true diazo-compound, but, when heated with concentrated potassium hydroxide, it is converted into the isomeric salt of phenylnitrosamine:

$$C_6H_5.N=N—OK \longrightarrow C_6H_5.NK—NO.$$

In a later article[3] Bamberger presents an additional piece of

[1] Ber. d. chem. Ges., **24**, 3255; **25**, 3190; **25**, 3505.
[2] *Ibid*, **26**, 514.
[3] *Ibid*, **27**, 584.

evidence in favor of the view that diazobenzenic acid has the formula $C_6H_5.NH.NO_2$, and indirectly that diazobenzene itself is a nitrosamine, $C_6H_5.NH.NO$. By treating aniline with nitrogen pentoxide he obtained diazobenzenic acid together with a number of other products. Its formation, according to Bamberger, takes place thus:

$2C_6H_5.NH_2 + N_2O_5 = 2C_6H_5.NH.NO_2 + H_2O$; a nitro-group being introduced into the amido-group.

Von Pechmann and Frobenius describe[1] experiments showing that, when benzoyl chloride acts upon alkaline solutions of aromatic diazo-compounds, nitrosamines are formed in which the benzoyl is in combination with nitrogen. This reaction, according to the authors, is most easily explained on the assumption that in the alkali salts the metal is linked to the nitrogen:

$C_6H_5.NNa.NO + C_6H_5.COCl = C_6H_5.N(COC_6H_5).NO + NaCl.$

Acetic anhydride acts in the same way giving acetyl derivatives of nitrosamines:

$$C_6H_5.NNa.NO + (C_2H_3O)_2O = C_6H_5.N(C_2H_3O).NO + NaC_2H_3O_2.$$

As the products thus obtained are identical with the compounds prepared by O. Fischer[2] by the action of nitrous acid on acid anilides, the constitution of the acetyl derivatives of the diazo-compounds is thus made clear. It follows from the above that aromatic amines, when treated successively with nitrous acid and acetic anhydride, yield identical products, independently of the order in which the reagents are applied. This indicates that the intermediate products in each case, for example, diazobenzene and acetanilide, have analogous constitutions, that is to say, that free diazobenzene is to be regarded as the anilide of nitrous acid, a conclusion already drawn by Bamberger as shown above. Further evidence in favor of this view is found in the fact that, by boiling an alkaline solution of a diazo-compound, a nitrite is formed to some extent. Assuming now that free diazobenzene is the anilide of nitrous acid, the isomeric hydroxide, $C_6H_5.N=N.OH$, appears as the analogue of the tautomeric forms of acid anilides. These are not stable in free condition, but only in the form of certain salts, for example, the imide chlorides. The following formulas exhibit the analogy:

$C_6H_5.NH.NO$	$C_6H_5.NH.C(CH_3)O$
$C_6H_5N:NOH$	$C_6H_5.N:C(CH_3)OH$
$C_6H_5.N:NCl$	$C_6H_5.N:C(CH_3)Cl$

If diazobenzene has the constitution, $C_6H_5.NH.NO$, and its alkali salts a similar constitution, nitrosamines should,

[1] Ber. d. chem. Ges., **27**, 651. [2] *Ibid*, **9**, 464; **10**, 959.

under proper conditions, show the reactions of alkaline solutions of diazo-compounds and, for example, give diazoamido-compounds with primary bases, and oxyazo-compounds with phenols. With nitrosanilides such reactions take place, but it is still doubtful whether they do with true nitrosamines. Thus, from nitrosoacetanilide and toluidine, diazoamidobenzene-toluene was obtained, acetic acid being split off:

$$C_6H_5N(COCH_3).NO + NH_2C_7H_7\ C_6=H_5NH.N:NC_7H_7 + C_2H_4O_2.$$

This reaction can be interpreted differently. It might, for example, be supposed that the nitrosanilide is first hydrolyzed, yielding acetic acid and diazobenzene, and that the latter then acts directly upon the toluidine forming the diazoamido-compound. This explanation appears improbable to the authors, for the reason that the acetyl group is held in the nitrosanilides much more firmly than the nitroso group. The analogy between the nitrosanilides and diazobenzene is observed also in their conduct towards phenol. In both cases oxyazo-compounds are formed. The experiment was made with acetyl-*p*-tolylnitrosamine and resorcinol, which yielded *p*-tolueneazoresorcinol and acetic acid according to the equation:

$$C_7H_7N(COCH_3).NO + C_6H_4(OH)_2 = C_7H_7N:NC_6H_3(OH)_2 + C_2H_4O_2.$$

The authors claim that their experiments have furnished new evidence in favor of the view that in alkaline solution the aromatic diazo-compounds can act as nitrosamines.

Von Pechmann and Frobenius confirm[1] the statement of Schraube and Schmidt that the yellow sodium salt from *p*-nitrodiazobenzene gives with methyl iodide *p*-nitrophenylmethylnitrosamine $C_6H_4(NO_2).N(CH_3).NO$, and they find that, when the silver salt is used instead of the sodium salt, a true ether of nitrodiazobenzene, $C_6H_4(NO_2)N:NOCH_3$, is formed. That the product has this formula appears from the following facts:

(1) When boiled with dilute acids it yields nitrogen and *p*-nitrophenol.

(2) When molecular quantities of the ether and of aniline are allowed to stand together for some time in alcoholic solution, yellow, silken needles of *p*-nitrodiazoamidobenzene, $C_6H_4(NO_2)N:N.NHC_6H_5$, separate.

(3) By treatment with phenol *p*-nitrobenzeneazophenol, $C_6H_4(NO_2)N:NC_6H_4OH$ is formed. The difference between the conduct of the silver salt and that of the sodium salt of *p*-nitrodiazobenzene is most easily explained by the assump-

[1] Ber. d. chem. Ges., **27**, 672.

tion that the former is an oxygen salt, $C_6H_4(NO_2)N:NOAg$, and the latter a nitrogen salt, $C_6H_4(NO_2)NNa.NO$.

While from the above it appears that the isodiazo salts can be converted directly into nitrosamines of secondary aromatic bases, $RNH.NO \longrightarrow R.NCH_3.NO$, the reverse process had not been accomplished. This Bamberger has now done.[1] When methylanilinenitrosamine is subjected to the action of fusing potassium hydroxide the methyl group is replaced by hydrogen, while the nitroso-group, strange to say, retains its place. The product is isodiazobenzene:

$$C_6H_5.NCH_3.NO \longrightarrow C_6H_5.NH.NO.$$

Thus far everything appears clear and simple. There are two varieties of diazobenzene, the true diazobenzene $C_6H_5N=NOH$, and isodiazobenzene, $C_6H_5.NH.NO$, the latter being in fact a nitrosamine. Similar differences exist between other diazo-compounds and corresponding isodiazo-compounds. But now comes Hantzsch with the somewhat startling announcement[2] that the two isomeric forms of diazo-compounds are, in fact, stereoisomeric. At the beginning of his article he lays down three theses which he then proceeds to justify by reason and by experiment. These theses are:

(1) There are two structurally identical forms of diazo-compounds. Both are represented by the well-known, general structural formula, $C_6H_5.N:N.X$.

(2) (a) These two forms are stereoisomeric in the sense of the space formulas:

$$\begin{array}{l} C_6H_5.N \\ \quad\| \\ X.N \end{array} \qquad \text{and} \qquad \begin{array}{l} C_6H_5.N \\ \quad\| \\ N.X \end{array}$$

and are *syn-diazo-compounds* and *anti-diazo-compounds*.

(b) The ordinary long-known diazo-compounds are *syn-diazo-compounds* corresponding to the first configuration. The isomeric diazo-compounds, which have proved to be structurally identical with these, and which are, in general, identical with the isodiazo-compounds, correspond to the second configuration. They are *anti-diazo-compounds*.

3. As regards the nature of the isodiazo-compounds the following may be remarked: There are undoubtedly isodiazo-compounds of the structural formula $C_6H_5.N:N.X$ (or $C_6H_5.N:N.OX$). But, further, the free isodiazo-hydrates, $C_6H_5.N_2OH$, which were discovered by Bamberger and by Schraube and Schmidt, and which they regarded as nitrosamines, $C_6H_5.NH.NO$, structurally isomeric with the true diazo-hydrates, $C_6H_5.N:N.OH$, are most probably not these

[1] Ber. d. chem. Ges., **27**, 1179. [2] *Ibid*, **27**, 1702.

structurally isomeric nitrosamines, but true diazo-hydrates. They are stereoisomeric anti-diazo-hydrates

$$C_6H_5.N$$
$$\|$$
$$N.OH.$$

Of course, everything depends upon the evidence. Let us follow Hantzsch in his reasoning. According to the ideas first advanced by Hantzsch and Werner in regard to the stereoisomerism of compounds containing nitrogen, stereoisomerism appears probable in the case of diazo-compounds. There is a close analogy between the oximes and the diazo-compounds as is shown by the formulas :

$C_6H_5.CH:N.OH$	$C_6H_5.N:N.OH$
Oxime.	Diazo-compound.

The latter may be regarded as derived from the former by the substitution of an atom of nitrogen for the group CH. Assuming that such substitution is possible we have the following parallel series :

I. *Geometric-isomeric Carbon Compounds. General Formula,* $R_1R_2C:CR_3R_4$.

Simplest structural formula RHC : CHR with the configurations of the

1. Cis-series.		2. Trans-series.
R.C.H		R.C.H
||	and	||
R.C.H		H.C.R.

Substitution of nitrogen for CH or CR would give :

II. *Geometric-isomeric Carbon-Nitrogen Compounds. General Formula,* $R_1R_2C:NR_3$.

Simplest structural formula RHC : NR with the configurations of the

1. Syn-series.	2. Anti-series.
R.C.H	R.C.H
||	||
R.N	N.R.

Most important representatives :

(a) Geometric-isomeric oximes of the structural formula $R_1R_2C:N.OH$;

(b) Geometric-isomeric hydrazones of the structural formula $R_1R_2C:N.NHC_6H_5$;

(c) Geometric-isomeric imido-compounds (anils) of the structural formula $R_1R_2C:N.C_6H_5$.

A further substitution of nitrogen for CH or CR would give :

III. *Geometric-isomeric Nitrogen Compounds. General Formula,* $R_1N:NR_2$.

Simplest structural formula RN : NR with the configurations of the

1. Syn-series.	2. Anti-series.
R.N	R.N
||	||
R.N	N.R.

Most important representatives:

(a) Geometric-isomeric diazo-compounds of the formula R.N : N.X.

(b) Geometric-isomeric azo-compounds of the formula R.N : N.R.

The parallel between the diazo-compounds and oximes was referred to above. It appears clearest when the free oximes are compared with the free diazo-compounds in the form of hydrates; the latter appear as oximes in which nitrogen has been substituted for CH:

Structural formula of the oximes (aldoximes) R.(CH) :N.OH;
Structural formula of the diazo-hydrates R(N) : N.OH.

According to Hantzsch, the evidence thus far presented has failed to show that the so-called isodiazo-compounds are nitrosamines. The formation of nitrogen ethers from the alkali salts certainly does not prove the correctness of this formula, as oxygen ethers are formed from the silver salts. On the other hand Hantzsch presents what he believes to be direct evidence showing the existence of isomeric diazo-compounds, in cases in which tautomerism is out of the question. Working with F. M. Perkin he thought that they obtained two diazo-amido-benzenes which must be represented by the formulas $C_6H_5.N:N.NH.C_6H_5$ and $C_6H_5.NH.N:NC_6H_5$, and these are plainly identical, and a difference appears possible only in terms of stereochemistry. But, unfortunately for this evidence, Bamberger,[1] has since shown that Hantzsch was in error in regard to these compounds and that they are, in fact, not isomeric. Still later Hantzsch[2] acknowledged his error. Hantzsch has shown, further, that two salts of the formula $C_6H_5.N:N.SO_3K$ can be prepared. When a diazo salt is treated with potassium sulphite, the first product is the new isomer:

$$C_6H_5.N:N.Cl + K_2SO_3 = C_6H_5.N:N.SO_3K + KCl.$$

This product is darker, orange-colored, and more easily soluble than the salt hitherto known. It is unstable, indeed explosive, and, under certain conditions, it is transformed into the isomeric salt. As its most important reaction, it exhibits the characteristic property of the true diazo-compounds; it unites with phenols in alkaline solution to form azo-dyes.

[1] Ber. d. chem. Ges., **27**, 2596. [2] *Ibid.*, **27**, 2968.

The isomeric, secondary salt is identical with the well-known salt first described by E. Fischer. It is bright yellow, more difficultly soluble than the primary salt and more stable. The most important difference between it and the isomeric salt is seen in its conduct towards phenols with which it does not unite to form azo-dyes.

These two salts cannot be isomeric in the sense in which the two potassium salts of diazo-benzene have been supposed to be isomeric. If they were, one would have the formula $C_6H_5.N:N.SO_3K$, and the other $C_6H_5.N(SO_3K):NO$, a supposition that appears absolutely untenable in view of the fact that one of these salts is easily transformed into the other.

Bamberger replies to Hantzsch in a long article[1] which may be summed up in one sentence taken from it: "The author (Hantzsch) has not furnished a particle of evidence of the existence of isodiazo compounds $C_6H_5.N:N.X$ or $C_6H_5.N:N.OX$. Not a single fact is known, in the field of diazo-compounds, that makes it necessary to adopt the principles of stereochemistry for purposes of explanation. The stereochemical formulas of diazo- and isodiazo-compounds have decided disadvantages as compared with the ordinary structural formulas." Bamberger claims that Hantzsch has not furnished any evidence that the two sulphonates, $C_6H_5.N:N.SO_3K$, are structurally identical, and points out that they may be represented respectively by the two formulas, $C_6H_5.N:N.O.SO_2K$ and $C_6H_5.N:N.SO_2K$. Meanwhile E. Fischer had suggested this possibility to Hantzsch, and the latter attempts to show[2] that the view previously taken by him is the more probable. Bamberger, however, replies,[3] maintaining still that the facts are far from proving that the two salts in question are stereoisomeric modifications. He admits the possibility that stereoisomerism may hereafter be observed among diazo-compounds, but holds that, at present, any assumption of stereoisomerism in this field is gratuitous. I. R.

The Recent Work of Moissan upon the Metallic Carbides.[4]

Wöhler showed that by the action of carbon on an alloy of calcium and zinc, a mixture of compounds was formed which yielded acetylene when treated with water. Lately Maquenne, following up the studies of Winkler on the reduction of the carbonates of the alkaline earths by magnesium, prepared

[1] Ber. d. chem. Ges., **27**, 2582.

[2] *Ibid*, **27**, 2099.

[3] *Ibid*, **27**, 2930.

[4] Bull. Soc. chim. (Paris) [3], **11**. For abstracts of former papers by Moissan dealing with research in this field, see this Journal, **13**, 374-378.

barium acetylide containing some barium hydride, which, on treatment with water, yielded acetylene mixed with 3-7 per cent. of hydrogen.

Moissan points out that while it has long been known that many fused metals can dissolve carbon, the compounds generally obtained consist of a solution of a metallic carbide in an excess of metal. To obtain definite crystallized carbides a higher heat is necessary than is obtainable in the ordinary furnace. By using his electric furnace Moissan can obtain a temperature of about 3500°, which suffices for the formation of these carbides.

If a mixture of 125 grams of quicklime with 70 grams of carbon (from sugar) is heated in a carbon crucible fifteen to twenty minutes with a current of 350 ampères and 70 volts, calcium acetylide is formed:

$$CaO + 3C = CaC_2 + CO.$$

The yield is 120–150 grams. The acetylide is a fused black homogeneous crystalline mass of easy cleavage. Single detached crystals are opaque and lustrous. Their density is 2.22. Calcium acetylide cannot be dissolved in any acid without decomposition. It is not acted on by hydrogen. Chlorine acts at 245° forming calcium chloride and carbon; bromine acts at 350°; iodine at 305°; oxygen at a red heat, forming calcium carbonate; sulphur at 500°, forming calcium and carbon sulphides; phosphorus and arsenic at a red heat, forming calcium phosphide or arsenide. Dry nitrogen, silicon, and boron, do not act at any temperatures tried, up to 1200°. Few metals act: neither sodium nor magnesium attack it at the temperature at which hard glass vessels fuse; iron does not act at a red heat, but at higher temperatures forms a mixture of carbides of calcium and iron, with an alloy of calcium and iron. Dilute acids act more readily than concentrated; hydrochloric acid yields calcium chloride and acetylene. If the acetylide is heated in a tube with anhydrous alcohol, calcium ethylate and acetylene are formed:

$$2C_2H_5OH + CaC_2 = (C_2H_5O)_2Ca + C_2H_2.$$

The most interesting action is that of water which at ordinary temperatures forms quantitatively acetylene and calcium hydroxide, thus furnishing the best method for the analysis of the compound.

Barium and strontium acetylides, BaC_2 and SrC_2, have the same physical and chemical properties as the calcium salt, and were made by Moissan in the same way.

Chemists have not hitherto succeeded in making any carbides of aluminium, and some have doubted the solubility of carbon in this metal. Moissan placed carbon boats, each

filled with 15–20 grams of aluminium, in the carbon tube of his electric reverberatory furnace;[1] a current of hydrogen was then conducted through the tube and the furnace heated five minutes with a current of 300 ampères and 65 volts. The current of hydrogen was continued while the furnace was cooling. On breaking the metallic contents of the boats, the mass of aluminium was found filled with lustrous yellow crystals. The aluminium was removed by treating the mass with concentrated hydrochloric acid at low temperature. The carbide can also be formed by the action of carbon on kaoline at the same temperature. The yellow crystals are of hexagonal form, transparent and lustrous. Some were 5–6 mm. in diameter.

Aluminium carbide is more stable toward most reagents than the carbides of the alkaline earths. At a dull red heat the action was as follows: Chlorine and bromine attack it slowly; oxygen acts with extreme slowness; phosphorus and nitrogen do not act at all, but sulphur attacks it with violence, forming sulphides of aluminium and carbon. Cold concentrated hydrochloric acid acts very slowly, dilute acid more quickly. Boiling concentrated sulphuric acid is reduced to sulphur dioxide. Water at ordinary temperatures decomposes the carbide quantitatively, but very slowly, into aluminium hydroxide and methane:

$$Al_4C_3 + 12H_2O = 3CH_4 + 4Al(OH)_3.$$

The reaction—which is hastened by heat but not by light—needs ten to twelve days for completion. Still it proved the best method for analysis.

This is the first methide known, and it seems strange to rank methane with acetylene, phosphine, and hydrogen sulphide as a weak acid.

Moissan suggests that aluminium methide may play a part in the formation of the methane which is constantly escaping from fissures in the earth's crust.

The fact that all of the carbides mentioned are formed at high temperatures by the action of carbon on metal oxides, and are decomposed by water, makes it probable that the carbon now taking part in vegetable and animal life was in the form of carbides at earlier geological epochs. The calcium and aluminium carbides would have been the widest spread and most important. The decomposition of the carbides of the alkaline earths by air at a red heat, forming carbonic acid, would explain the passage of carbon from the form of a solid carbide to the gaseous form of carbon dioxide, ready for assimilation by plant life.

[1] Compt. rend., **117**, 679.

In an article[1] on metallic chromium, Moissan speaks of two definite crystalline carbides of that element which he obtained by the action of carbon on chromium under varying conditions. The carbide Cr_3C_2 crystallizes in lustrous leaflets, little attacked by reagents, and not decomposed by water. The carbide Cr_4C crystallizes in lustrous needles, sometimes 1–2 cm. long. Moissan does not describe the properties of these crystals; hence the inference is that they resemble the carbide Cr_3C_2 in their stability toward reagents.

E. R.

NOTES.

Iodonium Bases.

Early last year a brief account was given in this Journal,[2] of some recent work by Victor Meyer and C. Hartmann on a new class of compounds containing iodine but no nitrogen. The principle substances then described were a base of the constitution, $\frac{C_6H_5}{IC_6H_4}>I.OH$, and salts derived from it, such as the iodide, $\frac{C_6H_5}{IC_6H_4}>I.I$, the chloride, $\frac{C_6H_5}{IC_6H_4}>I.Cl$, etc. Later the authors announced[3] that they had discovered a method by which they could prepare the mother-substance, of which the above-mentioned base is the monoiodo substitution-product, that is to say, the compound of the constitution, $\frac{C_6H_5}{C_6H_4}>I.OH$.

This could not be prepared by the substitution of hydrogen for iodine in the base first discovered. After many preliminary experiments the following method was devised: An intimate mixture of equivalent quantities of iodosobenzene and iodobenzene is shaken with moist silver oxide, by means of a shaking machine, and then filtered. The filtrate gives with potassium iodide an abundant precipitate of the new iodide, amounting to 83 per cent. of the mixture used, that is 93 per cent. of the theoretical yield. The following equation represents the reaction:

$$C_6H_5.IO + C_6H_5.IO_2 + AgOH = AgIO_3 + (C_6H_5)_2.I.OH.$$

As regards the nomenclature of the new compounds the authors remark: "The new iodide stands to iodobenzene in the same relation as *trimethylsulphonium iodide* to *methyl sulphide*, and as *tetramethylammonium iodide* to *trimethylamine*:

$N(CH_3)_3$ — Trimethylamine.

$HO.N(CH_3)_4$ — Tetramethylammonium hydroxide.

[1] In the same number of the *Bulletin*.

[2] This Journal, **16**, 233.

[3] Ber. d. chem. Ges., **27**, 502.

$S(CH_3)_2$
Methyl sulphide.

$HO.S(CH_3)_3$
Trimethylsulphonium hydroxide.

$I.C_6H_5$
Iodobenzene or phenyl iodide.

$HO.I(C_6H_5)_2$
Diphenyliodonium hydroxide.

They, therefore, call the mother-substance of the whole series, the compound $HO.IH_2$, *iodonium hydroxide* (corresponding to ammonium hydroxide, $HO.NH_4$) and designate the new iodide and hydroxide as:

$HO.I(C_6H_5)_2$
Diphenyliodonium hydroxide.

$I.I(C_6H_5)_2$
Diphenyliodonium iodide.

The new iodide crystallizes from alcohol in long yellowish needles that melt at 175°–176°, at the same time undergoing decomposition into iodobenzene:

$$I\begin{<}\begin{matrix}C_6H_5\\C_6H_5\\I\end{matrix}=C_6H_5I+C_6H_5I.$$

The free base obtained from the iodide by shaking it with moist silver oxide has a *strongly alkaline* reaction in water solution. The dilute water solutions can be kept for days without change. The chloride, $(C_6H_5)_2I.Cl$, bromide, $(C_6H_5)_2I.Br$, and pyrochromate $[(C_6H_5)_2I]_2Cr_2O_7$ are described.

The iodonium bases and their salts exhibit a marked resemblance to the derivatives of lead, silver, and especially *thallium*. The halogen compounds are precipitates which in color and solubility strongly suggest those of the metals named. The hydroxide and carbonate are soluble in water and give an alkaline reaction as in the case of thallium. This similarity raised the question whether the iodonium bases may not also give precipitates with hydrogen sulphide or ammonium sulphide. In fact, diphenyliodonium hydroxide was found to give a precipitate with ammonium sulphide looking exactly like freshly precipitated antimony sulphide.

In their last article[1] on the subject of iodonium bases the authors describe the following salts in addition to those mentioned above: The nitrate, $(C_6H_5)_2I.NO_3$; the acid sulphate, $(C_6H_5)_2I.HSO_4$; the acetate, $(C_6H_5)_2I.OC_2H_3O$; the periodide, $(C_6H_5)_2I.I+I_2$; and some double salts. A further investigation of the precipitate formed by ammonium sulphide in solutions of the salts of diphenyliodonium hydroxide has shown that it consists principally of the trisulphide, $(C_6H_5)_2I.S.S.S.I(C_6H_5)_2$. This decomposes readily thus: $[(C_6H_5)_2I]_2S_3=2C_6H_5I+(C_6H_5)_2S_3$.

[1] Ber. d. chem. Ges., **27**, 1592.

An investigation of the iodonium bases from a physiological point of view by Dr. Gottlieb, showed that their effects are similar to those produced by lead and thallium, and, in some respects, to those produced by ammonium bases. I. R.

On Diazomethane.

H. Von Pechmann[1] has succeeded in preparing the simplest conceivable organic diazo-compound, diazomethane, $CH_2\begin{matrix}\diagup\\\diagdown\end{matrix}\begin{matrix}N\\\vdots\\N\end{matrix}$, by treating nitrosomethylbenzoimide, nitrosomethylmethane, and other similar nitroso derivatives of methylamine with alkalies:

$$CH_3N\begin{matrix}\diagup NO\\\diagdown Ac\end{matrix} + NaOH = CH_2N_2 + H_2O + AcONa.$$

The product is a yellow gas. The yield is about 50 per cent. of the theoretical. While the compound at ordinary temperatures is a gas it is probably condensable by cold to a liquid. It is extremely poisonous. Owing to the difficulty of working with it the author has, for the present, confined himself to experiments with the ethereal solution. Towards acids the compound is very sensitive. The yellow ethereal solution is decolorized by them at once at ordinary temperatures with evolution of nitrogen. With iodine, diazomethane yields methylene iodide thus:

$$CH_2N_2 + I_2 = CH_2I_2 + N_2.$$

I. R.

The Composition of the Vapor of Calomel.

The determinations of the vapor-density of mercurous chloride made by Mitscherlich,[2] Deville and Troost,[3] Rieth,[4] and others, have all gone to show that the density found is only one-half that calculated on the basis of the formula Hg_2Cl_2. Odling, however, called attention[5] to the fact that calomel-vapor is capable of amalgamating gold-leaf, and Erlenmeyer[6] was able to corroborate this statement by more conclusive experiments. An investigation by Debray,[7] which seemed to lead to an opposite conclusion, was shown by Le Bel to be of little weight, since Debray had failed to note that at high temperatures the gold amalgam is dissociated and can, therefore, exist only for a few moments after the insertion of the cool

1 Ber. d. chem. Ges., **27**, 1888.
2 Ann. der Phys. Pogg., **29**, 139.
3 Compt. rend., **45**, 821.
4 Ber. d. chem. Ges., **3**, 666.
5 J. Chem. Soc., **3**, 211.
6 Ann. Chem. (Liebig), **131**, 124.
7 Compt. rend., **83**, 330.

gold-leaf into the hot vapor. The conclusion of Erlenmeyer that the decomposition $Hg_2Cl_2 = Hg + HgCl_2$, was complete, was declared by Debray, on the basis of later experiments, to be untenable, on the ground that the vapor on condensation yielded calomel as well as mercuric chloride and mercury.

The matter has, within the past year, been taken up by Victor Meyer and W. Harris, the results of whose investigation[1] are about as follows:

Gold-leaf is amalgamated by calomel-vapor at the moment of insertion, but on becoming hot returns to its original color. The temperature of vaporization of calomel is 357°. The vapor-density at 448° was found to be 8.215; at 518°, 8.169; calculated for $Hg_2Cl_2 = HgCl_2 + Hg$, 8.152. The first figure is the average of twelve, the second of eight determinations. Four experiments were made with a mixture in equivalent quantities of mercury and mercuric chloride; the average density was 8.267. In every case the residue left in the vessel, on cooling, was calomel.

On heating calomel, Meyer and Harris found that, whether a diaphragm was used or not, metallic mercury separated through its greater volatility and left a mixture of the two chlorides behind.

On inserting a stick of solid caustic potash into the vapor of calomel, an immediate deposition of mercuric oxide on its surface was noticed, precisely like that formed when the vapor is that of mercuric chloride. No deposit of mercurous oxide could be detected. To make sure that the mercuric oxide had not been formed through the decomposition of the black oxide at the temperature of the experiment, a stick of potash coated with mercurous oxide was subjected to the same temperature; the formation of mercuric oxide was not noticeable for 15–25 seconds; it then gradually changed from black to yellow. These experiments make it evident that the vapor of calomel consists of mercuric chloride and mercury, and that the mercurous salt is not volatile without decomposition. The formula of calomel must, therefore, according to Meyer and Harris be written Hg_2Cl_2.

Since the publication of the paper by Meyer and Harris, M. Fileti has called attention[2] to an investigation, an account of which[3] had been published in 1881, and in the course of which he had determined the vapor-density of calomel in the presence of the vapor of mercuric chloride. Although, according to Fileti, it was definitely proved that calomel-vapor was not dissociated under these conditions, nevertheless the density corresponded to the formula HgCl and not to the

[1] Ber. d. chem. Ges., **27**, 1482. [2] J. prakt. Chem., [2], **30**, 222.
[3] Gazz. chim. ital., **11**, 341

formula Hg_2Cl_2. Fileti bases his view of the non-dissociation of the vapor upon the fact that a tube plated with gold and kept cool by a current of cold water, shows no sign of amalgamation on insertion into the vapor of calomel when the vaporization has been brought about in the presence of mercuric chloride as above described. Accordingly there would seem to be no reason for assuming any formula for calomel more complex than HgCl. The dissociation of calomel-vapor when heated alone should therefore, according to Fileti, be represented by the equation

$$2HgCl = HgCl_2 + Hg,$$

and not by

$$Hg_2Cl_2 = HgCl_2 + Hg.$$

Victor Meyer has since[1] replied to this paper. His answer is that Fileti's experiment is of no value as a proof of the absence of metallic mercury from the vapor of calomel when that substance is heated in the presence of mercuric chloride. On cooling the mixture of the vapors of mercury and mercuric chloride—the two substances being present in equivalent proportions—his experiments had shown that pure calomel was deposited. If now an *excess* of mercuric chloride be present, there is practically no opportunity for metallic mercury at a low enough temperature to amalgamate gold, to come in contact with the cold metal tube. The cooling of the mixed vapors would result in the formation of the two chlorides of mercury only, entirely without admixture of the metal. To test this view, a mixture of mercuric chloride and mercury in the proportion of 3 : 1, was heated and the vapor allowed to come in contact with a gold-plated copper tube kept cool by a current of cold water : no amalgamation could be noticed. Whereas, when ammonium chloride was employed instead of the mercuric salt, an immediate and most marked amalgamation was produced. All the evidence, therefore, according to Meyer, leads to the view that calomel is not volatile without complete dissociation and, since its vapor-density is that of a mixture of equivalent quantities of mercuric chloride and mercury, that its formula must be written Hg_2Cl_2.

W. W. R.

A Sulphide of Tin Soluble in Ammonium Carbonate.

In the course of some experiments having for their object the preparation of tin absolutely free from arsenic, F. W. Schmidt[2] has obtained an oxysulphide of tin, which is readily soluble in ammonium sulphide. The substance can be pre-

[1] Ber. d. chem. Ges., **27**, 3143. [2] *Ibid*, **27**, 2739.

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pared as follows: A solution of stannous chloride is oxidized by warming and adding nitric acid; it is then evaporated to drive off at any rate part of the excess of acid, is diluted with water, and treated with hydrogen sulphide. The precipitated sulphide is washed, dissolved in concentrated hydrochloric acid, the solution diluted, filtered, and again treated with hydrogen sulphide, which then yields sulphide of tin free from arsenic sulphide. The precipitate is carefully washed and is then treated with a solution of ammonia; after standing for several days at the ordinary temperature, it is practically all dissolved. After filtration the ammoniacal solution is diluted and acidified with sulphuric acid, when an almost white precipitate is thrown down. This, when freshly deposited, dissolves completely in ammonium carbonate solution. On standing it becomes less soluble. Analysis showed the dry substance to be an oxysulphide of the formula Sn_2S_2O. The sulphide becomes yellow in color on standing exposed to the air and at the same time less and less soluble in ammonium carbonate. Eventually it becomes insoluble; but if the substance be redissolved in ammonia and again precipitated by addition of acid, the white voluminous sulphide is again obtained, completely soluble in the carbonate solution. The change which takes place on exposure to the air seems to be a loss of combined water and the parallel conversion of a voluminous deposit into one that is, relatively, very compact.

The bearing of this investigation upon the exact separation of the sulphides of tin and arsenic with the aid of ammonium carbonate solution, is evident. W. W. R.

Carbazide, CON_6, and Diurea, $(CO)_2(NH)_4$.

The first of these interesting compounds was made by Curtius and Heidenreich[1] from carbohydrazide, a crystalline primary hydrazine, formed by the action of ethyl carbonate on hydrazine hydrate in a sealed tube at 100°:[2]

$$CO<\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}+2N_2H_4=CO<\begin{matrix}NH-NH_2\\NH-NH_2\end{matrix}+2C_2H_5OH.$$

When the hydrochloride of this base is treated with sodium nitrite they react with ease:

$$CO<\begin{matrix}NH-NH_2-HCl\\NH-NH_2-HCl\end{matrix}+2NaNO_2=2NaCl+4H_2O+CO<\begin{matrix}N_2\\N_2\end{matrix}$$

Carbazide, as first formed, is a colorless oil which explodes violently if touched; by dissolving it in ether and allowing the ether to evaporate slowly, the carbazide is left in long crystalline needles which generally explode with violence if exposed

[1] Ber d. chem. Ges., **27**, 2684. [2] *Ibid*, **27**, 56.

to light, but can sometimes be kept for a time. The substance is extremely volatile and has a penetrating and suffocating odor like that of triazoic acid or that of phosgene. It is easily soluble in alcohol or ether. Saponified with alkali, it yields a triazoate and carbonic acid:

$$CON_6 + 2NaOH = 2NaN_3 + CO_2 + H_2O.$$

Treated with aniline it yields carbanilide and triazoic acid:

$$CON_6 + 2C_6H_5.NH_2 = 2HN_3 + CO{<}\begin{matrix}NH-C_6H_5\\NH-C_6H_5\end{matrix}.$$

These reactions prove the constitution of the substance which may be regarded as carbonic acid in which the hydroxyl groups are replaced by triazoic-acid residues, or as triazoic acid in which the hydrogen of two molecules is replaced by the bivalent group carbonyl.

Diurea is made from ethyl hydraziformate, a crystalline salt formed by the action of ethyl chlorformate on hydrazine hydrate:[1]

$$2CO{<}\begin{matrix}Cl\\OC_2H_5\end{matrix} + 3N_2H_4 = 2N_2H_4.HCl + \begin{matrix}NH-COO-C_2H_5\\|\\NH-COO-C_2H_5\end{matrix}.$$

Ethyl hydraziformate.

Ethyl hydraziformate heated in a sealed tube with hydrazine hydrate at 150°, yields diurea and alcohol:

$$\begin{matrix}NH-COO-C_2H_5\\|\\NH-COO-C_2H_5\end{matrix} + N_2H_4 = 2C_2H_5OH + \begin{matrix}HN-CO-NH\\|\quad\quad|\\HN-CO-NH\end{matrix}.$$

Diurea crystallizes in monosymmetric prisms, soluble with difficulty in cold water and in alcohol. It is a strong monobasic acid, decomposing carbonates; is very stable, but can be split into hydrazine and carbon dioxide by heating with concentrated hydrochloric acid in a sealed tube at 150°:

$$C_2N_4H_4O_2 + 2H_2O = 2N_2H_4 + 2CO_2.$$

The ammonium, barium, silver, and hydrazine salts of diurea were analyzed, as well as a benzal derivative,

$$C_2N_4H_2O_2.CH.C_6H_5,$$

which diurea forms with benzaldehyde. This benzal derivative is also a monobasic acid, as was shown by the analysis of its silver salt, $C_2N_4HAgO_2:CH.C_6H_5$. E. R.

Anhydrous Hydrogen Peroxide.

Hydrogen peroxide, which is practically anhydrous, has been prepared by Richard Wolffenstein[2] in the organic labora-

[1] Ber d. chem. Ges., **27**, 773. [2] Ber. d. chem. Ges., **27**, 3307–3312.

tory of the Technische Hochschule in Berlin. A 3-per cent. commercial solution of hydrogen peroxide was freed from all traces of alkalies, metallic sulphides, solid particles, and bodies of an indifferent chemical nature. This purified solution was concentrated on a water-bath under 68 mm. pressure to a solution containing 49.5 per cent. of hydrogen peroxide, the yield being almost quantitative. Under the ordinary atmospheric pressure a 20.2-per cent. solution was obtained, with a loss of only 12.9 per cent., when the operation took place on an oil-bath heated to 160°–170° C. If the experiment was so conducted that the solution to be concentrated rose only to 37° C., then a 54-per cent. solution was obtained, the yield being 75.5 per cent. This method is slow, however, and it is better to evaporate the solution directly on the water-bath, care being taken that the temperature of the hydrogen peroxide solution does not rise above 75° C. This method gives a 66.6-per cent. solution, but the yield is only 28.3 per cent. When a beaker was substituted for the evaporating dish a better result followed; *viz.*, a 64.7-per cent. solution with a yield of 56 per cent. This result seemed to prove that the loss in the experiment immediately preceding the last was partly due to actual volatilization of the hydrogen peroxide and not to decomposition as has hitherto been supposed. To further substantiate this hypothesis, solutions of different strength were heated in sealed tubes to 80° C. for two hours with the following results:

9.3	per cent.-solution.	96.9	per cent.	remained	undecomposed.
47.7	" "	82.5	"	"	"
48.0	" "	74.1	"	"	"
68.1	" "	74.05	"	"	"

These results led the author to attempt the direct distillation of hydrogen peroxide in a vacuum. For this purpose a 45-per cent. solution was further concentrated by extraction with ether to a 73.5-per cent. solution, and the latter was distilled from a water-bath under 68 mm. pressure. The distillate was collected in two fractions, one of which boiled at 81°–85° C. and was a 90.5-per cent. solution. This yielded by another fractionation a liquid boiling at 84°–85° C. under 68 mm. pressure and containing 99.1 per cent. of pure hydrogen peroxide.

This is practically anhydrous hydrogen peroxide. It is a clear, sirupy liquid, which does not wet a surface as easily as water; it is volatile in the air, and is acid to litmus; when brought upon the skin, it produces a prickling sensation and white spots, which, however, disappear after a few hours. It forms two hydrates, $H_2O_2 + H_2O$ and $H_2O_2 + 2H_2O$, which freeze at the temperature of a mixture of solid carbon dioxide and ether.

L. C. N.

Action of Soap as a Cleansing Agent.

An explanation of the action of soap as a cleansing agent has been furnished by a recent investigation by Krafft and Stern[1]. The older theory, based on the work of Chevreul, that the power of soap to dissolve fats is due to the free alkali produced by the decomposition of the salts of the fatty acids, which form the soap, has been opposed, of late, by the more modern view advanced by Rotondi (1883). According to the latter, water decomposes soap into insoluble acid salts and basic salts which remain in solution. These basic salts are the active cleansing agents. The work of Krafft and Stern confirms Chevreul's results and shows that basic salts are not formed. The action of water on the sodium salts of palmitic, stearic, oleic, and elaïdic acids was studied. Sodium palmitate was boiled with varying quantities of water and the mixture which separated out on cooling was analyzed. When 900 parts of water was used the bi-palmitate,

$$C_{16}H_{31}O_2Na.C_{16}H_{32}O_2,$$

was formed. The filtrate from the insoluble acid salt was treated with a mineral acid. Palmitic acid was not precipitated, therefore basic salts were not present. In a second experiment, when the filtrate was titrated with a standard acid, the amount of alkali found corresponded to the amount set free in the formation of the bi-palmitate. A hot solution of sodium palmitate was extracted with toluene. Pure palmitic acid was obtained. From these facts it follows that, in a hot dilute solution of sodium palmitate, a part of the salt is dissociated into free acid and free alkali. The presence of the acid in oily drops causes the cloudiness of the solution. When the solution cools, the free acid unites with some of the neutral salt to form the bi-palmitate, and the alkali remains dissolved. It is this free alkali on which the efficiency of soap depends. The action of water on the sodium salts of stearic and elaïdic acids is analogous to that on the palmitate. Sodium oleate dissolves with only slight decomposition in boiling water. J. F. N.

[1] Ber. d. chem. Ges., **27**, 1747.